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THE COLORS AND ABSORPTION-SPECTRA OF THIN METALLIC FILMS AND OF INCANDESCENT VAPORS OF THE METALS; WITH SOME OBSERVATIONS ON ELECTRICAL VOLATILITY.

BY WILLIAM L. DUDLEY.

Several years ago the writer began to investigate methods for obtaining metals in thin films, with a view to the study of the relations existing between their color by transmitted light and that emitted by their incandescent vapors; also to the study of their absorption-spectra. A number of methods were resorted to, for instance:

1. Volatilisation by boiling and condensation on glass;

2. Electro-deposition and removal of the "base" on which the metal is deposited by a suitable solvent;

3. Reduction of a salt which had been spread in a thin and uniform layer on the surface of a transparent base;

4. Volatilisation by the electric arc between terminals of the metal enclosed in a glass tube filled with an inert atmosphere; and

5. Volatilisation by the condensed electric spark under similar conditions.

Each method had its value in particular cases, but no one method seemed to be capable of universal application, although the last mentioned was generally applicable. I will describe briefly the various methods employed.

(1). Volatilisation by boiling was resorted to in dealing with potassium, sodium and lithium. Potassium, which had been freed from all mechanical impurities and hydrocarbons, was introduced into a glass tube filled with an atmosphere of hydrogen or nitrogen which was highly attenuated by a pump, and sealed. The portion of the tube in which lay the globule of metal was gradually heated over a Bunsen burner until the potassium boiled, when the tube was immediately withdrawn from the flame. The vapor of the potassium condensed in a thin film on the cooler portions of the tube, and exhibited in the thinnest parts colors by transmitted light ranging from violet to blue as the thickness increased, while by reflected light the film had the usual silvery metallic lustre of potassium. The film is not permanent. The brilliant colors gradually fade, until after some days they have completely disappeared, owing to the thin layer slowly drawing itself together into minute globules which to the unaided eye give to the whole surface a frosted appearance. By again heating the metal to boiling as before a new film can be produced.

Sodium and lithium were treated in the same manner as potassium. Sodium, however, gave a yellow-brown film, which was due to its action on the glass; the color was at first ascribed to the reduction of silica, but when lithium was treated in the same way the glass was also attacked, the color of the film being deep red-brown. The glass was permanently colored in each case, the metals having combined chemically with it, as one would naturally expect. The color conveyed by each was, however, a source of surprise, since it approached more or less closely, even under these circumstances, to that of its incandescent vapor. It may be accounted for in the same way as is gold "ruby" glass, *i. e.* is due to the presence of finely divided metal distributed through the glass. If thin gold leaf, which exhibits a fine green color by transmitted light, be spread out on a sheet of glass and heated to 316° or over, the color becomes red, and if the temperature has not been so high as to incorporate the gold with the glass, the green color may be restored by simply burnishing the surface.[1] The ruby color of the glass is held to be due to the gold in a finely divided state, and the colors given to glass by sodium and lithium may be due to the same cause. Many kinds of glass were

[1] Faraday, Phil. Trans. 1857, 145; also, his Experimental Researches in Chemistry and Physics.

employed—all, of course, without lead in their composition—and the effect was always the same.

(2). Electro-deposition is of limited application; gold films may, however, be readily produced, owing to the ease with which this metal is deposited; its resistance, too, to the action of acids making the separation of the film from the metal upon which it is deposited a simple matter.[1] A difficulty is encountered in this method in efforts to obtain films of proper thickness; this is, however, largely obviated by a method employed by Kundt,[2] in which he obtains a wedge-shaped film by placing the cathode horizontal in the bath and the anode very near, and perpendicular to, the surface of the cathode. Thus the film tapers out in a very thin edge. Arsenic deposited on glass by decomposing arsine may prove a good surface upon which to make the deposits, as it could easily be dissolved off of the film by sodium hypochlorite or some other suitable solvent. I have never tried it, however, as I found that other methods served my purpose in most instances.

(3). The reduction of a thin film of the metallic salt was found unsatisfactory for various reasons, and was not employed, although films of platinum could be obtained quite easily, giving a purple color by transmitted light.

(4). The electric arc between terminals of the metal to be volatilised proved successful in a few cases. The terminals were inserted into a glass tube filled with an inert atmosphere, and brought in contact for an instant. The metal was suddenly vaporised and thrown upon the glass, but was usually granular or powdery, of a black or brown color, altogether unsatisfactory, owing to its discontinuous character.

(5). The condensed spark between two points of the metal enclosed in a glass tube, exhausted, or filled with an inert atmosphere highly attenuated, serves well in many cases. For descriptions of this method in detail I refer to papers by Wright,[3] Hartley[4] and Crookes.[5] Hartley, however, volatilised the metals in the air, and consequently only a few of the films were metallic. The facility with which metals volatilise by this method varies very much:

[1] Outerbridge, Paper by Eggleston, Trans. Am. Inst. Min. Eng. **7**, 91.

[2] "Ueber die Brechungsexponenten der Metalle," Ann. der Phys. Wied. **34**, 469.

[3] "On the Production of Transparent Films by the Electrical Discharge in Exhausted Tubes," Am. J. Sci. (3) **13**, 49; **14**, 169.

[4] "On Films produced by Vaporised Metals and their Applications to Chemical Analysis," Proc. Roy. Soc. **46**, 88.

[5] "On Electrical Evaporation," Chem. News **63**, 287.

those of low atomic weights showing, as a rule, more resistance than the heavier metals to the action of the spark. According to Crookes, this power of resistance does not increase regularly as the atomic weight decreases. No relationship has yet been discovered between the degree of electrical volatility and any known constant. Some relationship might be discovered if the volatilisation were carried on under such conditions of temperature and pressure as would most likely insure similar molecular conditions in each case. This might possibly involve the melting-point, as well as the atomic weight, as a factor.

If the order of the electrical volatility of the metals as found by Crookes be compared with Lothar Meyer's curve of atomic volumes, it will be found that the volatile metals lie at or near the minima of the curves, close together on the ascending sides in the periods IV, V and VII, alternating from one to the other. Magnesium and aluminium, which are practically non-volatile, lie on the descending side of period III. Aluminium, which is less difficult to volatilise than magnesium, is nearer the minimum of the curve. The metals given in the order of their electrical volatility alternate in the periods as follows:

Metal.	Comparative Electrical Volatility.—Crookes.	Period.
Pd	108.	V
Au	100.	VII
Ag	82.68	V
Pb	75.04	VII
Sn	56.96	V
Pt	44.00	VII
Cu	40.24	IV
Cd	31.99	V
Ni	10.99	IV
Ir	10.49	VII
Fe	5.50	IV

A thin, reguline and coherent film of a metal transmits light of a color remarkably similar to that emitted by its incandescent vapor. The color of the vapor of a metal varies with the temperature. Just above its boiling-point the vapor of sodium is purple; at incandescence, yellow. The vapor of potassium is green; at incandescence, violet. Silver in distilling gives off a blue-white vapor, while that volatilised by the electric arc passing between silver electrodes emits yellowish-green light. The color of the film obtained in many cases agrees very well with that of the

incandescent vapor. In some instances, however, there is no similarity (see table below), a fact which is probably due to failure to obtain the proper conditions for the volatilisation and deposition. The perfection and continuity of the deposit is easily destroyed by very slight changes in the conditions. For instance, the aluminium film deposited by Wright by condensed sparks was brownish, while that observed by Fleming,[1] which resulted from the volatilisation of an aluminium connection in an overheated incandescent lamp, was of a "fine blue" color in the thinnest portions.

The color of the incandescent vapor of a metal is the resultant of the colors of the various rays emitted, and depends on the number and intensities of these rays; the color can therefore be fairly predicted on examining a table of the wave-lengths and relative intensities of the spectral lines of the metal.

I give below a table containing a number of metals, in which is given the color of the films by transmitted light, and the color of the incandescent vapor as observed and as indicated from the spectral lines. The authorities are given as far as possible. In some cases I have been unable to find any mention of the color of the incandescent vapor, although I am sure it must have been observed. In such cases I put my own name.

The color of a film will vary somewhat with the thickness, but as far as I have observed the colors extend over a very limited portion of the spectrum. Each metal possesses a strong tendency toward a characteristic color which is produced when the film is as thick as it can be to transmit any light.

Absorption Spectra of Metallic Films.

Many of the films which corresponded closely in color to the incandescent vapor of the respective metals were examined carefully as to their absorption spectra by throwing a powerful beam of white light through them. If the same molecular condition existed in the film as in the incandescent vapor we would expect to have the same absorption. In other words, the dark lines of the absorption spectrum of the film should coincide with the bright lines of the emission spectrum of the incandescent vapor. I found in every case, however, that the films gave simply general absorption, no bands or lines being indicated.

School of Chemistry, Vanderbilt University, *February*, 1892.

[1] Discourse delivered at the Royal Institution, The Electrician **24**, 393.

METAL.	COLOR OF FILM.	OBSERVER.	COLOR OF INCAND. VAPOR.	OBSERVER.	Color of Incand. Vapor as indicated by spectrum.
Gold	Pinkish, violet, blue, blue-green	Faraday, Wright and others			
Heated to 316°	Green	Crookes and others	Green	Dudley	Green
" on glass	Red	Faraday and Wright			
	Red				
Silver	Deep blue	Wright	Blue	Stas	
			Yellow-green in electric arc	Dudley	Yellow-green
Copper	Green	Wright, Fleming	Green	Dudley	Green
Aluminium	Fine blue	Fleming			
	Brownish	Wright	Green-blue	Dudley	Green-blue
Bismuth	Gray-blue	Wright	Blue, slightly greenish	Dudley	Blue-green
Platinum	Blue-gray	Wright			
	Purple	Dudley	Blue (?)	Dudley	Blue
Palladium	Smoky brown	Wright	Green	Deville and Debray (?)	Green
Lead	Smoky brown inclining toward olive	Wright	Blue	Dudley	Blue
Zinc	Gray-blue, less deep than Ag, deeper than Bi.	Wright	Green-blue	Dudley	Green-blue
Cadmium	Gray-blue, about same as Zn, slightly less intense	Wright	Green	Dudley	Green
Magnesium	Gray blue, similar to Zn and Cd, but less clear	Wright	Green	Wright	Green
Tin	Brown-gray	Wright	Blue (?)	Dudley	Blue-green (?)
Iron	Neutral tint with faint tinge of brown	Wright	Green-blue	Dudley	Green-blue
Nickel	Gray or brown-gray	Wright	Blue-green	Dudley	Blue-green
Cobalt	Gray or brown-gray	Wright	Green-blue	Dudley	Green-blue
Tellurium	Dull purple	Wright	Golden yellow	Gernez	Orange-yellow
Potassium	Blue-violet	Dudley	Violet	Davy	Violet
Sodium heated on glass	Brown-yellow	Dudley	Yellow	Davy	Yellow
Lithium heated on glass	Dark brown-red	Dudley	Red	Arfvedson (?)	Red

THE VOLUME LAG AND ITS BEARING ON MOLECULAR CONSTITUTION.

By C. Barus.

1.[1] In studying the relation between melting-point and pressure I came across a series of phenomena, the nature of which it was necessary to elucidate before the general problem could be attacked. I found the pressure necessary to solidify a substance decidedly greater than the pressure at which it again passes into the liquid state, *caet. par.* At first sight it seemed reasonable to suppose the differences so obtained could be referred to heating effects on compression and to cooling on expansion; but the magnitude of the pressure interval observed is often too large for this interpretation (palmitic acid). Solidification and fusion are almost instantaneous, provided pressure vary by a step exceeding the lag limit. Moreover, the simple statement given does not bear inspection. If the substance be liquid at pressure p and temperature t, then immediately after solidification by pressure the conditions are $p + \delta p$ and $t + \delta t$. If now $p + \delta p$ be reduced to p, and the substance remain solid, its temperature must be t', where $t + \delta t > t' > t$. The converse holds on liquefying. Hence, virtually, the substance is liquid at a lower temperature and higher pressure, and solid at a higher temperature and lower pressure than the mean values, and hence the occurrence of lag is really accentuated by the thermal discrepancy.

Relative to the character of these phenomena, pressures admit of a much more finely graded variation than temperatures. By applying pressures isothermally it may therefore be possible to demonstrate the generality of occurrences which have a counterpart in the retarded solidification of a substance either from fusion or from solution. Aside from these inferences, the interpretation to be given can be decided by a time criterion. If the maximum pressure at which the substance just remains liquid persistently exceeds the minimum pressure under which it just remains solid, *caeteris paribus*, then the observed phenomenon is a true volume lag.

[1] The paragraphs are not numbered consecutively, but in agreement with a larger article. Let me say here that throughout the paper the terms volume lag and hysteresis are used in ways essentially alike.

I may conveniently insert a few special examples from my notes here. Caprinic acid is easily cooled below its melting-point (30°). To solidify it in this condition (say at 29°) requires at least 400 atm. To remelt it at the same temperature would only be possible under negative pressure, *i. e.* under a definite deduction from the internal pressure of the substance. Similarly, but more remarkably, thymol, though melting, say at 50°, can easily be undercooled to 28° and less. At 28°, at least 500 atm. are necessary to solidify it. In spite of the larger interval of undercooling, larger pressure is essential for solidification than in the preceding case. Again, para-toluidine, melting at 45°, is only solidified at 28° (undercooled) by pressures of about 500 atm. Obviously, these phenomena are independent of heating by compression.

3. My experiments[1] on melting-point and pressure differed from those of my predecessors, inasmuch as I made the volume changes due to pressure acting at constant temperature, a criterion of the state or condition of fusion. The substances were enclosed in glass capillary tubes, kept at the desired temperature by a vapor-bath (boiling tube of the kind described in detail elsewhere).[2] It was frequently necessary to boil under diminished pressure in order to obtain convenient temperatures of solidification. The upper end of the capillary being suitably closed, the lower was put in connection with a large Cailletet force-pump.[3] A measured pressure was thus applied at pleasure by pushing the thread of mercury in the lower end of the capillary against the substance. The way in which the mercury thread advances is characteristic. So long as the substance is liquid, the thread rises directly in contact with the substance, and capped by an unbroken meniscus. When solidification commences the meniscus is soon broken and pointed, and the thread eventually runs up between walls of the solid compressed substance. When pressure is withdrawn again, it frequently happens that small threads of the mercury column have actually broken off. The reason for this behavior is at hand: on solidifying, the column contracts markedly from the axis of the tube radially outward, leaving the core in a vacuous, spongy state. Into this central sponge the additional pressure forces the finer filament of mercury by breaking the dissepiments. Usually a good criterion for the occurrence of solidification is given by the

[1] The apparatus is shown in Am. J. Sci. **39**, 6 (1890).
[2] Bull. U. S. G. S. **54**, 88 (1889).
[3] Made both by Ducretet and the Société Genevoise. Capacity, 1000 atm.

optical change from clear to opaque. Thus, in case of paraffin, a white thread shoots, as it were, through the axis of the originally clear capillary.

4. The present paper was written some two years ago,[1] and I then provided a full series of results of the volume lag observed in palmitic acid, naphthalene, monochloracetic acid, and paraffin. With my present facilities and experience, however, I am able to improve on this work considerably. I have therefore here withdrawn the original data, merely stating that I have them in hand and that they were obtained by the capillary-tube method just described. Data sufficient for my present purposes are given in my more recent work on the continuity of solid and liquid.[2] To fully exhibit the hysteresis, volume should be mapped out as a function of time, using pressure as a parameter. The curves so obtained are persistently asymmetrical when the isothermal march is made alternately from liquid to solid and from solid to liquid.

Discussion.

8. The first point of view from which these data are to be studied is that of the thermodynamic cycle and relative to $\int pdv$. It also involves a consideration of James Thomson's doubly-inflected isothermals. The discussion, however, is best omitted here, and will be made elsewhere.

9. Before proceeding further, it is expedient to insert a definite view as to the underlying causes of the liquefaction of a gas and of the solidification of a gas, or a liquid. I shall employ the current chemical terminology, and explain my meaning more fully in the course of the paper, §§22, 25. My hypothesis is that change of the state of aggregation is brought about by, and is evidence of a corresponding change of the (cohesive) valency in one or more of the constituent atoms of the substance. Valencies are added in successively decreasing intensity. More sharply:

(1) A liquid or gas solidifies whenever, in consequence of changes of the physical or chemical environment (temperature, stress external or internal, etc.), the valency of the constituent atoms is sufficiently increased to admit of the permanent construction of a continuous tridimensional chain, the type structure and the molecular weight of which (solid) are each a multiple of the given structure and molecular weight.

[1] Cf. Am. Journal **38**, 408 (1889).

[2] Am. Journal **42**, 140 *et seq.* (1891).

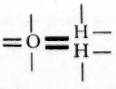
(2) A gas liquefies whenever, in consequence of changes of environment, the valency of one or more of the constituent atoms is sufficiently increased without affording means for the permanent construction of the tridimensional chain in question.

Suppose the molecule of a gas be called free. Then the molecule which is free to move along a wall of similar molecules (and such may be the case at the surface of some liquids and solids) may be said to have lost one degree of freedom; if it is constrained to move in the angle between two such walls, it has lost two degrees of freedom. Finally, with the same understanding in mind, the solid molecule has lost three degrees of freedom. Thus, as will appear more clearly below, the three states of aggregation are related to the three dimensions of space.

The criterion by which (1) and (2) are obtained is compressibility; for I have merely supposed that when compressibility suddenly and phenomenally increases (as it does at liquefaction and solidifying points), the inherent cause is an increase of valency, whereby external pressure is now reënforced by internal pressure.

It does not follow from (1) and (2) that a fluid may not exist below the corresponding liquefying or solidifying points. Elsewhere[1] I inferred that, as regards isopiestic thermal expansion, the liquid and the solid, as well as the gas, obey certain ideal laws, which may be conceived to hold good on both sides of the points in question, quite apart from the usually gratuitous hypothesis of polymerism. Seeing that a given state of aggregation maintains its labile equilibrium through a wide range of changes of condition (cf. §1), one calls to mind certain results of the hydraulic experiments of Osborne Reynolds. Cf. §25.

10. Some illustration of the preceding paragraph is desirable. For instance, it is impossible to construct the tridimensional chain out of $O''H'$. Nor is this possible[2] with $O^{IV}H'$ or $O''H'''$. With $O^{IV}H'''$, the solid chain, if possible, would necessarily be an exceedingly complex structure. With $O^{VI}H'''$, a symmetrical in two dimensions, possessing hexagonal symmetry, may be made from the type structure



[1] Proceedings Am. Acad. **26**, 315 (1891).

[2] The possibility of trivalent, pentivalent, etc., hydrogen is discussed by Geuther (Jenaische Ztschr. (2) **6**, 119). Cf. Lothar Meyer, **9**, 333 (Breslau, 1884).

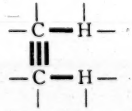
and for $O^{x}H^{vii}$, the same structure is possible in three dimensions. In the diagram, principal affinities are indicated by heavy lines, added affinities by light lines. They may be verbally distinguished as molecular and cohesive affinities, respectively.

Before reaching this extreme stage, a number of possible types have been passed, any one of which may possibly characterise the liquid molecule.

The conception thus gained of the gaseous and the solid states is clear-cut. The conception of the liquid states is apparently vague. It is at most a transitional stage. This, however, appears to me to be an advantage. It is in keeping with what is usually implied in the term liquid. The liquid molecule is constantly undergoing changes as regards the number of individuals which make up a single nomadic colony, without breaking up the type molecules out of which the colony is put together. The external effect of the exchange of the superfluous valencies, as it were, is exhibited in the cohesion of liquids. It determines the conditions of miscibility and of solution. It is further active in capillarity; §19.

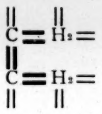
Note that, compatibly with the hypothesis given, a liquid is by no means necessarily a conductor of electricity. Cf. §9.

11. Evidence in favor of the view here advocated is given by the existence of any homologous chemical series, each member of which may in general occur in the three states of aggregation. If $A_l B_m C_n \ldots$ be any compound, and if the valency of each atom be cohesively increased $2x$ (following the order 1, 3, 5, 7 .... or 2, 4, 6, 8 ...), then there will be $2x(l+m+n)$ new bonds to combine with the $2x(l+m+n)$ new bonds of each of the contiguous molecules, to form a suitable tridimensional chain, without breaking the integrity of the original molecule of the gaseous state. More generally, $2x$ may be regarded different for each atom. Thus, for instance, solid acetylene may be typified by



where molecular affinities are denoted by heavy lines, and each light line (cohesive affinity) may be x or x'...fold, for carbon

and hydrogen, respectively. Similarly, solid ethylene is typified by



In the same way the character of solid isomers or of allotropic differences is retained. Supposing all the atoms accounted for, the negation of an increase of cohesive valency would necessitate a passage of $3C_2H_4$ into $2C_3H_6$ or into some higher homologue. This, however, is quite beyond the power of mere liquefaction or of solidification, generally speaking.

13. The views stated in §9 apply equally well whether solidification takes place after fusion or after solution. They suggest the function of water of crystallisation in many cases of solidification. In such instances, the (cohesive) valencies of the atomic constituents both of the water and of the dissolved salt have increased under the conditions stated in §9, (1), in such a way as to admit of the construction of the solid framework.

14. Instances of the availability of the present views in accounting for the properties of colloidal solutions, and for analogous phenomena in sedimentation, have been given elsewhere.[1] The ejection of dissolved gases by most liquids on solidifying is an allied example.

16. It follows, from §9, that molecules near the surface will be least favorably situated for stability; §18. In quiescent friction the conditions of occurrence seem to be such that time is given the molecules at the surface of contact of two bodies to interlock; §9.

17. It is the immediate result of §9 that when the valencies are reduced by heat to those which appertain to the gaseous state, the construction of a solid chain or of a liquid chain is impossible under any pressure. This begins to occur at Andrews' critical temperature. Again, when the valencies are reduced by heat to those which appertain to the liquid state, the construction of a tridimensional chain is equally impossible under any pressure. This suggests a lower critical temperature,[2] or, in other words, an eventual continuous passage from the solid to the liquid state by pressure.

[1] Barus and Schneider, Ztschr. phys. Chem. **8**, 289 (1891); Am. Journal **42**, 366-67 (1891).
[2] Cf. §4.

18. It was stated, §18, that surface molecules are probably least stable, since it is here that the cohesive affinities must unite among themselves in a way different from the body of the chain. This suggests the occurrence of volatilisation, evaporation, and greater tendency to break up in those parts. Viscosity, on the other hand, is the physical expression of internal imperfections of the solid chain.

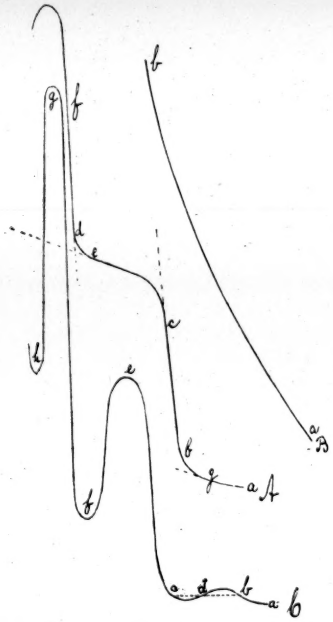
19. Again, the state of the surface may be considered in relation to capillarity; §10. The free affinities at contiguous surfaces are available for combination. At Andrews' critical temperature, the absence of marked capillary phenomena[1] demonstrates the absence of a possible solid or liquid chain. This is in accordance with §17. According to Hannay and Hogarth,[2] solution by no means ceases at the critical temperature. It is to be remarked, however, that neither is the gaseous molecule here exclusively present, since the lag (§§20, 21) has not wholly disappeared, nor is the critical temperature of a solution identical with that of the solvent.

20. The next step in the present considerations is the interpretation of lag phenomena as intimated in §8. My endeavor is to find a suitable lag mechanism. The variation of molecular force p_x with the mean distance apart x of the molecules acted on, may be represented by the horizontal push necessary to move a heavy point frictionlessly along a curve in a vertical plane. If a_x be the angle which the tangent at any point P of such a curve makes with the horizontal, then $p_x = g/\tan a_x$ is the horizontal force necessary to hold the point of weight g in equilibrium at P. Hence $a_x = \tan^{-1} g/p_x$ is the inclination to be given the curve at every point P whose abscissa is x, in order that motion along the curve in question may reproduce any stated variations of p_x. Finally, the position of P with reference to the vertical, *i. e.* its height above some fixed horizontal datum line, expresses the molecular potential energy under the given conditions of compression; §24. Similarly, the kinetic energy of the point may be utilised; for it is clear that when a_x lies between $\pi/2$ and π, p_x will be negative; and if negative pressure is excluded from consideration, it follows, from the principle of conservation, that whenever increasing a_x passes through $\pi/2$, molecular energy will change

[1] Mendeleeff, Pogg. Ann. **141**, 618 (1870).

[2] Hannay and Hogarth, Nature **120**, 82 (1879); Proc. Roy. Soc. Lond. **30**, 178 (1880); Chem. News **41**, 103 (1880).

from potential to kinetic. In how far negative values of a_x, corresponding to reëntrant figures, cannot be disregarded, will presently be stated.



In virtue of the occurrence of lag, the curve of motion will be harmonic. The annexed figure represents the series of phenomena here in question, apart from dimensions which cannot be clearly reproduced in the drawing. The mean distances between contiguous molecules are denoted by abscissæ. The curve *A* is first to be considered. Suppose it to start from *a*, the pressures or horizontal forces necessary to move it along the curve constantly increase until the point *c* is reached. From here on pressure, if kept constant, is in excess, and hence the point moves onward as far as *d*. To move it further, pressure must again

increase. Suppose now that after arriving at *d*, pressure is decreased. The point will at first move but slightly until in its retrograde march *e* is reached. After this, if pressure decreases further, the point will at once fall to some position *g*. For the purpose of the present diagram this kinetic energy of the point is disregarded.

Here, therefore, is the mechanism for a lag. Along the branch *agc* the substance is fluid, along *df* it is solid, and *ced* represents the transitional state from liquid to solid. The phenomenon is a temporary lag. Its occurrence is evoked by pressure, and after pressure has reached the original value at *a*, the effect of the lag is nil, since the point is also at *a*.

Manifestly the character of the curve *A* depends on temperature. Suppose temperature to be raised sufficiently above the corresponding critical point of the substance; then the lag will have wholly disappeared, and compression will take place along some curve *B* without harmonic contour.

21. Again, let temperature be decreased. Then the temporary lag *ced* of the curve *A* will become more pronounced in its harmonic curvature, and take some form *C*. To bring out the character of this diagram it would be necessary to apply pressure negatively, a problem experimentally impossible unless the whole phenomenon be exhibited by heat. For the sake of fixing ideas, however, suppose the substance at the low temperature in question to be imponderable. Suppose, too, that by some ideal means the individual molecules are all kept at the required distance apart, so that there is no nuclear condensation. Then, as pressure is applied, the point representing the changes of state when molecules approach each other will move along a curve *C*. There will be lag at *bdc* coincident with the passage from gas to liquid, and lag at *ef* coincident with the passage from liquid to solid. The lags so encountered, *i. e.* by these ideal means, will, however, be permanent, and therefore be an advanced state of the lag given in *A*; for the point remains in the valley after pressure is withdrawn.

In substances which, like thymol, can be undercooled, it is actually possible to produce a permanent lag corresponding to *cef* of the curve *C*, as was pointed out in §1. Explosion of a gas mixture like OH_2 by pressure alone is an allied instance.

Negative values of a_x corresponding to negative pressures are introduced by such substances as expand on solidification. The considerations here presented are peculiar; for, in a march of the

kind just described, *i. e.* with continual volume reduction, the liquid-solid lag would not at all appear.

22. The question now arises whether the two lags specified are the only ones which would occur in a general march of the kind here specified; in other words, has the curve any characteristic prolongation to the right and to the left? The first question is easily answered. Let successive constant temperatures at which condensations take place be selected, so that the body is kept in the field of the successive changes. In a passage toward the right the conditions of dissociation are encountered; and there must be a corresponding lag, permanent under suitable temperature conditions, in that region. Does the curve C terminate on the left at g? I believe that if solid matter is sufficiently compressed there must ultimately occur another lag of high-pressure order. Under proper conditions of temperature this extreme lag will be permanent, and will represent the passage of the given atom into the next consecutive of a series of atoms of increasing atomic weights. This is shown at gh in the figure. Again, toward the extreme right and beyond the field of dissociation, if the process of analysis be pushed further, another region of permanent lag will be passed through, representing the transfer of the given atom into the next consecutive of a series of atoms of decreasing atomic weights.

It will be noticed that the occurrence of lag is coexistent with the occurrence of cohesive affinities, as stated succinctly in §9.

23. Having thus supposed that affinities may be grouped in different orders, that primitive affinities are active in the atom, and that the coherence of the atom occurs in virtue of a volume lag of high-pressure order, these views account for vast aggregations of atoms of like kind. They are the products of a given order of lag.[1] The views also suggest a uniform scheme for the successive evolution of atoms, and are therefore in harmony with the periodic classification of elements. In general, a law of distribution is implied, by which the occurrence of any given dimension of ultimate particle is specified.

24. If it be supposed that each atom is wholly or partially surrounded by a molecular field of attraction, of definitely circumscribed dimensions and of equally definite contour, the occurrence of hysteresis necessarily accompanies any marked change of volume. There may be a series of such fields of force, either distinct, or symmetrically within each other. From this interpre-

[1] The laboratory being the interior of a sun or planet, for instance.

tation the diagram *C* at once follows. It was stated, §20, that the vertical height of the point in moving frictionlessly along the curve, above some fixed datum, is the expression of its potential energy. Hence, if the bounding surface of any field be a region of maximum potential relatively to the space on either side of it, the lag is permanent. If the bounding surface be a region at which the space-rate of change of potential is pronounced but does not pass through zero, the lag is temporary. It follows that chemical combination, change of state from gas to liquid, from liquid to solid, are successive stages of a periodically recurring volume lag. It follows also that the pronounced harmonic character of the space variation of molecular force at low temperatures gradually flattens out, and finally quite loses the said harmonic character at very high temperatures. Finally, the cohesive affinities of §9 may each correspond to special and distinct fields of atomic force; or they may result from the invasion by an atom, of the unoccupied space of a relatively large field of molecular affinity.

24*a*. I have attempted to associate these fields of force with an ether environment kept in a dynamically structural state by vibrating corpuscles (atoms or molecules); I have also given some consideration to the known behavior[1] of the vortex atom; but all this is far beyond the scope of the present paper, in which it is merely my object to see whether something may not be gained by supposing cohesive forces and affinities to be essentially the same in kind but differing in their respective orders of intensity.

25. It is in place, finally, to enumerate some other lags, and to refer them to the type lag of §§20, 21. Among these, phenomena of retardation at melting- and boiling-points, retarded fusion, undercooling, retarded condensation, superheating, are prominent. They have been virtually included in the preceding paragraphs, and therefore need not be touched upon again. The same is true of supersaturation in case of solution.

Lag phenomena are clearly observable in case of metals subjected to stress. By applying tractions, alternately increasing and decreasing between wide limits, Ewing[2] demonstrated the occurrence of lag thermo-electrically. In an earlier paper of Cohn[3] a similar method is pursued with the same results. Quite recently

[1] J. J. Thomson: A treatise on the motion of vortex rings. Macmillan, 1883, pp. 71 to 124.
[2] Ewing, Phil. Trans., London, 2, 361 (1886). [3] Cohn, Wied. Ann. 6, 385 (1879).

O. Schumann,[1] availing himself of Braun's[2] deformation phenomena, investigated a new lag by measuring the electrical resistances of a stretched helix of nickel wire.

The same class of phenomena are exhibited with singular clearness in case of magnetisation. They were first definitely pointed out and studied by Warburg,[3] though the questions had been elucidated by Fromme[4] and by Auerbach.[5] Ewing[6] made them the subject of an elaborate and independent research. Iron is operated on by magnetic fields alternately increasing and decreasing between stated limits, and the resulting induction compared with the intensity of the field at each stage of progress.

In studying the magnetic behavior of stretched and twisted nickel wire, Nagaoka[7] (and, I believe, Wiedemann, though I cannot now find the experiments after much searching) obtained definite cyclic variations due to torsion.

In all these cases the effect of stress is a lag of the nature of that described in curve *A*. Molecules, in favorable positional relations, are urged either into or out of the molecular fields of force of contiguous molecules, and the change of structure resulting is indicated mechanically, electrically or magnetically.

To these instances the remarkable discovery made by Osborne Reynolds[8] in studying the flow of liquids in pipes is to be added, since it is through this that a deeper insight into hysteresis may possibly be gained. According to Reynolds, "... if there were a critical velocity at which, for any disturbance whatever, the water became stable, this velocity was much less than that at which it would become unstable for infinitely small disturbances; or, in other words, suggesting that there were two critical values for the velocity in the tube, the one at which steady motion changed into eddies, the other at which the eddies changed into steady motion."

26. I have carried these considerations into much greater detail by applying them to electrical and magnetic phenomena, but the above paragraphs suffice to exhibit the point of view taken. It has been my endeavor to frame a working hypothesis which shall not be at variance with known facts of physics or chemistry, and which shall be sufficiently flexible to imply clear-cut conditions for the series of volume phenomena which I am investigating.

[1] Schumann, Wied. Ann. **38**, 256 (1889). [2] Braun, Wied. Ann. **37**, 97, 107 (1889).
[3] Warburg, Wied. Ann. **13**, 141 (1881). [4] Fromme, Ibid. **4**, 76 (1878); Ibid. **13**, 318 (1881).
[5] Auerbach, Ibid. **14**, 308 (1831). [6] Ewing, Phil. Trans. of London, **2**, 523 to 640 (1885).
[7] Nagaoka, Phil. Mag. (5), **27**, 117 (1889).
[8] Reynolds, Phil. Trans., London, **3**, 935 (1883); cf. p. 957.

ON CITRONELLONE, AN UNSATURATED FATTY ALDEHYDE.

By Edward Kremers.

In a paper read before the American Pharmaceutical Association in 1887 I presented a preliminary chemical examination of the citronella oil of commerce, with a review of the botanical and chemical literature of the different andropogon oils. In connection with this review, the fact was repeatedly pointed out that more or less confusion existed regarding the origin and composition of these oils. From my remarks on the "Production of the Oil" it could easily be inferred where the causes for such discrepancies were to be sought. So long as the manufacture of these products remains in the hands of ignorant natives, commercial articles sold under the same name may or may not be identical. It is therefore useless, under these conditions, to criticise the results of one investigator when they differ from those of another. The prime object of examining the andropogon oils at present must be to separate and study carefully the chemical characteristics of the substances they contain. It is only after knowledge has been thus attained that we shall be able to ascertain the exact composition of the various oils in question, having been distilled by reliable men, and from grasses identified by experts. This being accomplished, we can demand that the commercial oils be thereafter of uniform composition.

Since 1887 two chemists have taken up the subject of the andropogon oils: Mr. Frank D. Dodge, whose results have been published in this journal,[1] and Dr. F. W. Semmler.[2] I do not wish to compare the results obtained by Mr. Dodge with mine, for the above mentioned reason. Others have carried the comparison of our results to a point well-nigh ridiculous. But I object if Mr. Dodge and others compare the aldehyde bodies obtained by us, for my aldehyde by analysis was shown to possesss the formula $C_7H_{14}O$, whereas Mr. Dodge assigned to his aldehyde the formula $C_{10}H_{18}O$. As to the "citronellon" of Dr. Semmler, I would state that German melissa oil is a very questionable article. Dr. Bertram, in a private communication, has kindly informed me that the firm of Schimmel & Co. have never been able to obtain more than

[1] This Journal **11**, 456; **12**, 553.

[2] Ber. d. chem. Ges. **24**, 208.

traces of an oil from German balm. The term "citronellon" has been applied rather indiscriminately to aldehyde-like bodies from various oils. The "citronellon" examined by Dr. Semmler was isolated by him from citronella oil, whereas the bulk of commercial citronellon is obtained from the oil of *Eucalyptus maculata*, var. *citriodora*.[1]

Though there may be but little doubt regarding the identity of "citronellon" from various sources, yet it would be better to ascertain the facts before making any general statements. The literature of volatile oils is sufficiently complex indeed, and it should be our endeavor to simplify it rather than to add to its complexity.

The substance which has furnished the subject for this preliminary paper is the so-called *citronellon* from the oil of *Eucalyptus maculata*, var. *citriodora*. It was isolated from the oil by the chemists of Messrs. Schimmel & Co., Leipzig, and was generously given me for investigation.

The citronellone from this source is a colorless oily liquid of a lemon-like odor not at all disagreeable. Its specific gravity is 0.875 at 17.5°, and 0.871[2] at 20°. It rotates the ray of polarised light to the right 7.127° in a 1-dm. tube. Hence $[\alpha]_D = +8.18°$. The citronellone used in excess in the oxidation experiments with alkaline permanganate solution, after distillation with water vapor and drying over calcium chloride, possessed a specific gravity of 0.866 at 20.5°. In this case $[\alpha]_D = +8.220°$. Fraction 92°-95°, obtained by distilling citronellone under a pressure of only 15 mm., had the specific gravity 0.8632 at 20°. In a 2-dm. tube it rotated the ray of polarised light 15.858° to the right. Hence $[\alpha]_D = +9.18°$.

An attempt to distil the crude citronellone under ordinary pressure resulted in an entire failure. The following fractions were collected:

A = 98°–105° — a small quantity.
B = 195°–210° — less than one-third.
C = 215°–220° " " "
D = 280°–310° " " "

Fraction A developed upon standing an agreeable minty odor. Fraction B possessed a mixed odor; specific gravity 0.875 at 21°; $[\alpha]_D = +6.81°$. Triturated in a mortar with a molecular quantity of sodium acid sulphite and a few drops of water, a solid dry mass resulted which soon became almost odorless. Fraction

[1] Schimmel & Co., "Bericht," Oct. 1890, p. 21. [2] 0.873 at 15°.

C resembled B. Fraction D was a yellowish liquid of decided fatty odor; specific gravity about 0.902 at 22.5°; rotatory power in a 1-dm. tube about −3.455°. Treated with sodium acid sulphite like fraction B, it combined but partially with the salt. *It is noteworthy to observe the change in the action upon polarised light.*

Under a pressure reduced to 15 mm. but very little came over below 92°; about one-half came over between 92°–95°, and about one-third between 95°–97°. The mercury then rose quickly to 110°, when there remained in the flask a viscid yellow liquid.

The citronellone recovered from the oxidation experiments with permanganate, after being dried over calcium chloride, yielded the following results upon analysis:

I. 0.1475 gram gave 0.1718 gram H_2O = 0.01908 gram H, and 0.4178 gram CO_2 = 0.11394 gram C.

II. 0.1618 gram gave 0.1825 gram H_2O = 0.02027 gram H, and 0.4565 gram CO_2 = 0.12450 gram C.

III. 0.1064 gram gave 0.1240 gram H_2O = 0.01377 gram H, and 0.3007 gram CO_2 = 0.082009 gram C.

The following results were obtained from fraction 92°–95° distilled under a pressure of 15 mm.:

IV. 0.3102 gram substance gave 0.3310 gram H_2O = 0.03677 gram H, and 0.8781 gram CO_2 = 0.23948 gram C.

V. 0.2300 gram substance gave 0.2458 gram H_2O = 0.02731 gram H, and 0.6475 gram CO_2 = 0.17659 gram C.

VI. 0.3064 gram substance gave 0.3180 gram H_2O = 0.03533 gram H, and 0.8583 gram CO_2 = 0.23408 gram C.

VII. 0.2573 gram substance gave 0.2727 gram H_2O = 0.03030 gram H, and 0.7230 gram CO_2 = 0.19718 gram C.

	Calculated for		Found.	
	$C_{10}H_{18}O$.	$C_{10}H_{20}O$.	I.	II.
C	77.92	76.92	77.24	76.94
H	11.69	12.82	12.93	12.52

	III.	IV.	V.	VI.	VII.
C	77.07	77.20	76.77	76.39	76.63
H	12.94	11.85	11.87	11.53	11.77

These results on the whole do not agree better for $C_{10}H_{18}O$ than for $C_{10}H_{20}O$. However, the chemical behavior of the substance demands the adoption of the former formula. Analyses V. and VII. I have reason to consider the best, and the results calculated from these correspond fairly well with the formula $C_{10}H_{18}O$.

Citronellone and Bromine.

Citronellone readily decolorises bromine; 10 cc. citronellone, dissolved in 30 cc. glacial acetic acid and kept cold by ice, decolorised not quite 3 cc. bromine. The equation

$$\underbrace{C_{10}H_{18}O}_{154} + \underbrace{Br_2}_{160} = C_{10}H_{18}Br_2O$$

requires 2.8 cc. bromine. This proves more conclusively than the determination of the molecular refraction of a substance not chemically pure, that there is a double bond in the molecule, and that the formula therefore must be $C_{10}H_{18}O$, and not $C_{10}H_{20}O$.

The bromine addition-product is unstable and could not be obtained in a crystalline condition. Upon standing, the liquid blackened and hydrobromic acid was given off. Heated with an alcoholic solution of potassa, bromide of potassium was abundantly precipitated. The product was distilled with water vapor. The aqueous distillate possessed an agreeable minty odor. By extraction with ether, a few cubic centimetres of an oil were obtained which had a decided peppermint odor. Most of the oil had been resinified, and was not volatile with water vapor. A repetition of the experiment upon a somewhat larger scale yielded about 10 cc. of oily distillate, which upon redistillation was resolved chiefly into two fractions, boiling from 200°–210° and from 210°–220° respectively. These fractions have a decided peppermint odor, a characteristic property which has been produced in various reactions. This substance promises to be of some interest and will be further examined.

Citronellone and Sodium Acid Sulphite.

The citronellone under consideration was separated from the other constituents of the eucalyptus oil by means of its crystallisable sodium acid sulphite compound.[1] From this it was regenerated with the aid of sodium carbonate. That the compound had not suffered any change was readily shown by the fact that it again combined with sodium acid sulphite. The observation made by the chemists of Schimmel & Co., that the union of the two compounds is accompanied by a considerable rise in temperature, can also be confirmed. If molecular quantities of citronellone and sodium acid sulphite are triturated in a mortar, the latter

[1] Schimmel & Co., "Bericht," Oct. 1890, p. 21.

will dissolve in the former, and upon the addition of a few drops of water the emulsion-like liquid will congeal. This method of preparing the addition-product is not connected with the loss caused by the use of a solution of the sodium acid sulphite. An attempt to add two molecules of sodium acid sulphite failed.[1] When to the citronellone a hot concentrated solution of sodium acid sulphite (two molecules to one of citronellone) was gradually added, a crystalline magma resulted which dissolved in more of the solution. It was then heated for several minutes on a water-bath. Upon cooling, a mass of crystals separated, which were freed from mother-liquid and dried on porous plates. This product was recrystallised from hot water, and the resulting crystals were dried as before. These air-dried crystals lost but from 0.15 to 0.3 per cent. of their weight when kept in a desiccator for a week. The sulphur was estimated by fusing with potassa and nitre, dissolving the product in water and precipitating the sulphuric acid as barium salt. To purify the barium sulphate it was fused with sodium carbonate, the mass dissolved in water, and the sulphuric acid again precipitated with barium chloride.

I. 0.4418 gram substance yielded 0.3807 gram $BaSO_4 = 0.0522$ gram S.

II. 0.5995 gram substance yielded 0.4675 gram $BaSO_4 = 0.0641$ gram S.

Calculated for		Found.	
$C_{10}H_{18}O\,NaHSO_3$.	$C_{10}H_{18}O(NaHSO_3)_2$.	I	II.
12.40 per cent.	17.67	11.81 per cent.	10.69

Citronellone and Hydroxylamine.

A condensation-product of these two substances was obtained by allowing hydroxylamine hydrochlorate and sodium bicarbonate to react upon an alcoholic solution of citronellone until carbon dioxide was no longer liberated, and then heating the mixture on a water-bath. The filtrate from the sodium chloride was allowed to evaporate spontaneously, but no crystals resulted. The oily

[1] Comp. Heussler, Ber. d. chem. Ges. **24**, 1805; also, Dodge, This Journal **12**, 553. Dodge obtained from the aldehyde isolated from lemon-grass oil a compound with sodium acid sulphite, to which he assigned "the tentative formula $C_{10}H_{16}O.2NaHSO_3.4Na_2SO_3.50H_2O$." From the "dry salt" he obtained by analysis 22.48 per cent. sulphur, whereas the formula requires 22.6 per cent. Now the much simpler formula $C_{10}H_{18}O(NaHSO_3)_2$ requires 20.68 per cent. sulphur. The "citriodoric aldehyde" from lemon-grass oil, no doubt, has two double bonds. Perhaps a reaction takes place with this aldehyde similar to that Dr. Heussler has observed in the case of cinnamic aldehyde, although an analogous compound could not be obtained thus far from citronellone.

liquid which separated was distilled under ordinary pressure, but decomposed, hydroxylamine being given off. An attempt to distil it under greatly diminished pressure was more successful. Water came over at first, and then, under a pressure of 12 mm., two-thirds of the product distilled over between 128°–133°. During the distillation crystals formed in the condensing-tube, but afterwards redissolved. The distillate was set aside in a cold place, but even after weeks no crystals reappeared. It has not yet been analysed. The oxime—for such it apparently is—takes up bromine: from solutions in ether and in glacial acetic acid the addition-product separated as a viscid oil; from the solution in petroleum-ether acicular crystals separated, not in sufficient quantity, however, to be further investigated. Condensation with phenyl-hydrazine has thus far given even less satisfactory results.

Oxidation of Citronellone with Ammoniacal Silver Oxide.

Citronellone was oxidised in the same way with ammoniacal solution of silver oxide that Semmler oxidised the aldehyde $C_{10}H_{18}O$ from oil of balm ("Melissenö"), and the aldehyde $C_{10}H_{18}O$ from citronella oil.[1] These substances he chooses to call "citronellon," and to regard them as identical with the "citronellic aldehyde" of Dodge[2] and with the "citronellon" of Schimmel & Co.,[3] although he had not experimented with the "citronellon" from eucalyptus oil to which Schimmel & Co. first applied the term "citronellon," and for which it should be reserved until the identity of these various aldehydes, $C_{10}H_{18}O$, from different sources has been proved.

The silver salt was obtained from the solution of the sodium salt as a white, curdy precipitate, and is by no means characteristic in appearance. The dried salt was analysed with the following results:

I. 0.2128 gram substance yielded 0.3417 gram $CO_2 = 0.09319$ gram C, and 0.1297 gram $H_2O = 0.01441$ gram H.

II. 0.3720 gram substance yielded 0.1420 gram Ag.

	Calculated for $C_{10}H_{17}O_3Ag$.	Found.
C	43.32 per cent.	43.79 per cent.
H	6.14 "	6.77 "
Ag	38.99 "	38.17 "

[1] Ber. d. chem. Ges. **24**, 208. [2] This Journal **11**, 462. [3] Loc. cit.

Oxidation of Citronellone with Permanganate.

After a number of experiments, the following proportions were found to give the best results: To a solution of 12 grams of potassium permanganate in about 500 cc. of water, 12 cc. (*i. e.* an excess) of citronellone were added. The mixture was heated on a water-bath in a flask connected with a reflux condenser. When repeatedly shaken, the reduction of the permanganate was complete in less than an hour. The excess of citronellone was distilled off with water vapor, the remaining liquid filtered, and the filtrate evaporated on a water-bath. From 315 grams citronellone, 122 grams, or 38.7 per cent., were recovered;[1] 193 grams were oxidised.

The aqueous filtrate, containing the potassium salts of the acids formed by the oxidation, upon evaporation yielded two crops of crystals, chiefly oxalate and carbonate. To the mother-liquid dilute sulphuric acid (1:5) was added in slight excess; potassium sulphate was precipitated, and the liquid separated into an oily and an aqueous layer. The oily acid (112 grams) was of viscid consistency and of a reddish color. Attempts to prepare the sodium, calcium and barium salts directly yielded results not very satisfactory. When distilled under ordinary pressure a part of the crude acid came over between 300°–305°, but it was largely decomposed. When distilled under diminished pressure (reduced by 22 in.) an aqueous acid distillate came over first, but even under these conditions the contents of the flask soon underwent decomposition. The aqueous fraction when redistilled boiled between 100°–105°, and this distillate gave reactions for formic acid with ferric chloride, silver nitrate and mercuric chloride.

Distillation with water vapor was then resorted to. The acid distillate, from which no oil separated, when neutralised with soda also gave reactions for formic acid. The residue in the flask was perfectly clear—all the acid having gone into solution—and was shaken with ether; upon evaporation of the ether, a viscid liquid of slightly reddish color remained. When distilled (the pressure being reduced by 22 in.), water came over first, then

[1] More dilute solutions of permanganate apparently attacked the citronellone molecule more radically, since a larger percentage could be recovered unchanged. When 12 grams of citronellone were oxidised with 10.5 grams permanganate in 500 cc. of water, 55.5 per cent. of the citronellone was recovered. The same results were obtained twice. When 12 grams citronellone were oxidised with a solution of 21 grams of permanganate in 500 cc. of water, in one experiment 40.5 per cent., in another only 30.3 per cent. of citronellone was recovered by distillation with steam.

about two-thirds of the oil at 220°, when decomposition set in and the distillation was interrupted. The distillate was viscid, but colorless. Dried in a desiccator over calcium chloride, it yielded upon analysis the following results:

I. 0.4943 gram substance gave 0.9945 gram CO_2 = 0.27122 gram C, and 0.3830 gram H_2O = 0.04255 gram H.

II. 0.3682 gram substance gave 0.7514 gram CO_2 = 0.20492 gram C, and 0.2918 gram H_2O = 0.03242 gram H.

III. 0.2860 gram substance gave 0.5873 gram CO_2 = 0.16017 gram C, and 0.2267 gram H_2O = 0.02518 gram H.

	Calculated for $C_{10}H_{18}O_5$.	Calculated for $C_{10}H_{20}O_4$.	Found. I.	Found. II.	Found. III.
C	55.04	55.82	54.86	55.65	56.00
H	8.25	9.80	8.60	8.80	8.80

The results from I. would agree better with the formula $C_{10}H_{18}O_5$; the increase in the percentage of both carbon and hydrogen, however, in II. and III. indicates that moisture was still being given off. *A priori* considerations also would make the formula $C_{10}H_{20}O_4$ more probable. This supposition was strengthened, as will be seen, by the composition of the silver salt. The sodium salt obtained from this acid was crystalline; the silver salt prepared from the sodium salt was obtained as a white flocculent precipitate, and when exposed for some time to light did not blacken. The dried salt when analysed gave the following results:

I. 0.1738 gram substance yielded 0.2452 gram CO_2 = 0.06687 gram C, and 0.0860 gram H_2O = 0.00955 gram H.

II. 0.2465 gram substance yielded 0.3415 gram CO_2 = 0.09313 gram C, and 0.1242 gram H_2O = 0.01380 gram H.

III. 0.2027 gram substance yielded 0.2818 gram CO_2 = 0.07685 gram C, and 0.1037 gram H_2O = 0.01152 gram H.

IV. 0.0760 gram substance yielded 0.0275 gram Ag.

V. 0.2061 gram substance yielded 0.0748 gram Ag.

	Calculated for $C_{10}H_{17}O_5Ag$.	Calculated for $C_{10}H_{19}O_4Ag$.	Found. I.	Found. II.	Found. III.	Found. IV.	Found. V.
C	36.92	38.58	38.47	37.78	37.91	...	...
H	5.23	6.10	5.49	5.59	5.68	...	...
Ag	33.23	34.72	...	...	...	36.18	36.29

The solution of the ammonium salt of this acid, prepared by neutralising the acid with dilute ammonia, when evaporated on a water-bath gave off a rather toxic odor. The solution became

viscid and brownish, and would not crystallise. A silver salt, however, was prepared which became only grayish on exposure to light, and of which two silver estimations were made:

I. 0.2205 gram substance yielded 0.0965 gram Ag = 43.76 per cent.

II. 0.1893 gram substance yielded 0.0835 gram Ag = 44.10 per cent.

Apparently the ammonia not only neutralises the acid, but also effects other changes which will require special study.

The aqueous acid liquid, resulting from the addition of dilute sulphuric acid to the solution of the potassium salts which remained after the separation of the oily acid layer, was also distilled with water vapor. The acid distillate was neutralised with sodium bicarbonate, the solution evaporated, and the residue extracted with hot absolute alcohol. Several crops of sodium salt were thus obtained, small yet handsome prisms resulting in one case. From one of these crops a silver salt was obtained as a white curdy precipitate, which soon darkened and, upon standing in the desiccator, underwent decomposition. The first silver estimation yielded 39.7 per cent. Ag, the second 43.9 per cent., and the third 62.2 per cent. This precipitate probably consisted of a mixture of the silver salt mentioned above, together with the silver salts of lower fatty acids, *e. g.* formic acid. This question, however, deserves to be further investigated, especially since in one of the earlier experiments a silver salt obtained in the same manner was analysed, with the following results:

I. 0.2745 gram substance yielded 0.3072 gram CO_2 = 0.08378 gram C, and 0.1100 gram H_2O = 0.01222 gram H.

II. 0.2425 gram substance yielded 0.2727 gram CO_2 = 0.07437 gram C, and 0.0990 gram H_2O = 0.0110 gram H.

III. 0.3020 gram substance yielded 0.1471 gram Ag.

	Calculated for			Found.		
	$C_8H_9O_2Ag$.[1]	$C_6H_{11}O_2Ag$.	$C_6H_{11}O_3Ag$.	I.	II.	III.
C	28.70	32.28	30.12	30.52	30.66	...
H	4.30	4.93	4.60	4.45	4.53	...
Ag	51.67	48.43	45.18	...	...	48.70

No satisfactory formula could be calculated from these results.

[1] Semmler (Ber. d. chem. Ges. **24**, 209) states that the aldehyde $C_{10}H_{18}O$ from balm oil, when oxidised, yields isovaleric acid, and bases upon this fact his structural formula. He does not, however, furnish a single analytical proof.

The solubility of the non-volatile acid in water and ether suggested the treatment of the aqueous acid liquid with ether after the volatile products had been removed by distillation with water vapor. The separated ethereal layers, upon evaporation of the ether, yielded a reddish, viscid acid liquid which resembled that obtained from the original solution of the potassium salts upon the addition of sulphuric acid. Its ethereal solution does not decolorise bromine. It is precipitated from its aqueous solution by sodium acid sulphite, but apparently does not combine with this salt. No satisfactory results have thus far been obtained with phenyl-hydrazine or with benzoyl chloride. These experiments, however, are to be repeated with purer material as soon as this can be obtained, for it is necessary to ascertain the nature of the two additional oxygen atoms before the compound is oxidised any farther. That they are not present in the form of carboxyl oxygen is shown by the silver salt. *A priori* one would expect them to be present as hydroxy oxygen, two hydroxyl groups having been added in place of the double bond.

In conclusion I desire to render thanks to Messrs. Fritzsche Bros., who have kindly furnished the material for these investigations, which are by no means completed and will be continued.

PHARMACEUTICAL LABORATORY, UNIVERSITY OF WISCONSIN, *January*, 1892.

PROTEIDS OR ALBUMINOIDS OF THE OAT KERNEL.

SECOND PAPER.[1]

BY THOMAS B. OSBORNE.

In a paper on the proteids of the oat kernel, published in this journal,[2] the writer described a globulin obtained from the oat kernel by extraction with a 10-per cent. sodium chloride brine heated to 65° C. (Preparation **20**). It was shown that this globulin differs from that extracted by the same brine at 20° C. both in properties and composition, and that on cooling the warm-saturated solution of this body in dilute sodium chloride brine, crystals

[1] Read at the meeting of the National Academy of Sciences in New York, Nov. 10, 1891. From advance sheets of the Report Conn. Agri. Expt. Station, 1891.

[2] This Journal **13**, 406; also Report Conn. Agri. Expt. Station, 1890.

were several times obtained—once in the form of rhombohedra and at other times in the form of octahedra.

This globulin has been further investigated, and the results obtained are the main subject of this paper.

Proteid derived from the "Albuminate."

Preparations "**21**," "**22**" *and* "**23**."

When the oat proteids brought into solution in cold brine[1] are precipitated by saturating the extract with ammonium sulphate, a considerable part of this precipitate is always found to have lost its solubility in the salt-solution by conversion into a form called by Weyl "an albuminate" (Preparations **15** and **16**). In this state it is soluble in a 1-per cent. solution of sodium carbonate.

On treating ten pounds of freshly ground oats with brine, precipitating the filtered solution by saturating with ammonium sulphate, and extracting the precipitate thus obtained with brine, it was found that a very large part of the globulin originally dissolved was converted into the so-called "albuminate." After washing the latter thoroughly with brine to free it completely from the unchanged globulin, it was dissolved in a 1-per cent. sodium carbonate solution. About two-thirds of this solution was then treated with carbon dioxide for three hours, whereby a heavy white precipitate settled out. This precipitate was collected on a filter and allowed to drain overnight. The next morning it was found to have become transparent and gummy about the edges.

This precipitate was now completely soluble in salt-solution, and had all the properties of the globulin (**20**) previously obtained from the hot sodium chloride extract. The entire precipitate was then dissolved in 1 litre of brine and dialysed for four days, during which time all but a trace of the substance separated out. The proteid thus precipitated was seen under the microscope to consist of spheroids of about $\frac{1}{10}$ mm. diameter or less, similar to those obtained by cooling a warm solution of the globulin. After filtering off, washing with alcohol, ether and absolute alcohol, 21 grams of the air-dried material were obtained. This substance was completely soluble in brine, and was precipitated therefrom by diluting with water, by saturating with sodium chloride, or by

[1] Unless otherwise specified, "brine" and "salt-solution" are to be understood in this paper to signify aqueous solutions of very pure sodium chloride, containing 10 per cent. NaCl, used at common temperatures.

adding minute quantities of hydrochloric, nitric or acetic acid. In the entire absence of salts, extremely small amounts of the acids just named dissolved the proteid instantly and completely, but the addition of a little sodium chloride precipitated it from this solution, the extent of the precipitation depending on the relative quantities of the acid and salt present. The precipitation was complete when certain proportions of salt and acid were used. Addition of strong soda-lye to the solution of the proteid in dilute acid gave a heavy precipitate which dissolved but slowly in excess of soda, although the final mixture contained over 25 per cent. of sodium hydrate. Addition of copper sulphate to this alkaline solution gave the biuret violet. With Millon's reagent and with nitric acid the usual proteid reactions were obtained. Alcohol containing a minute amount of free acid dissolved the substance completely. Its composition was found to be as follows:

OAT PROTEID *derived from Sodium Carbonate Solution of the "Albuminate."—Preparation* **21.**

			Ash-free.	
	I.	II.	I.	II.
Carbon	52.28	..	52.30	..
Hydrogen	6.98	..	6.98	..
Nitrogen	17.86	17.73	17.86	17.73
Sulphur	0.69	..	0.69	..
Oxygen	..	..	22.17	..
Ash	0.03	..	..	..
			100.00	

Ash.—0.6759 gram substance, dried at 110° C., gave 0.0002 gram of ash = 0.03 per cent.

Carbon and hydrogen.—0.4610 gram dried substance gave 0.887 gram CO_2 = 52.28 per cent. C, and 0.3220 gram H_2O = 6.98 per cent. H.

Nitrogen, I (Dumas' method).—0.3474 gram dried substance gave 52.15 cc. N at 13° C. (barometer 768.2 mm. at 23° C.) = 17.86 per cent. N.

II (Kjeldahl method).—1.0108 grams dried substance gave ammonia = 21.8 cc. HCl sol. (1 cc. = 0.00822 gram N) = 17.73 per cent. N.

Sulphur.—0.7695 gram dried substance gave 0.0380 gram $BaSO_4$ = 0.0052 gram S = 0.69 per cent.

In all respects save one, this substance behaved exactly like the globulin obtained by extracting ground oats with hot sodium chloride solution. The latter proteid dissolved to a turbid solution in cold, and to a perfectly clear solution in hot distilled water. So far as the usual methods of analysis show, the two bodies are identical in composition, as is seen from the following figures:

	Globulin extracted from oats by hot sodium chloride solution —average of two analyses. Preparation **20.**	Globulin derived from sodium carbonate solution of "albuminate." Preparation **21.**
Carbon	52.22	52.30
Hydrogen	6.98	6.98
Nitrogen	17.82	17.86
Sulphur	0.77	0.79
Oxygen	22.21	22.17
	100.00	100.00
Ash	0.19	0.03

Another preparation of this substance was made by dissolving a second portion of the "albuminate" in 2-per cent. sodium carbonate solution, precipitating with carbon dioxide, washing thoroughly with water, dissolving in brine and diluting the solution with a large amount of water. The final, snow-white precipitate was filtered off and, after washing with alcohol and ether, weighed eleven grams. Its properties are exactly the same as those of **21**, except that it is slightly soluble in hot distilled water. Its composition, as determined by analysis, here follows:

OAT PROTEID *derived from Sodium Carbonate Solution of the "Albuminate."—Preparation* **22.**

		Ash-free.
Carbon	51.98	52.05
Hydrogen	6.92	6.93
Nitrogen	17.83	17.85
Sulphur } Oxygen }	..	23.17
Ash	.13	..
		100.00

Ash.—0.5437 gram substance, dried at 110° C., gave 0.0007 gram ash = 0.13 per cent.

Carbon and hydrogen.—0.5789 gram dried substance gave 1.1030 grams CO_2 = 51.98 per cent. C, and 0.3609 gram H_2O = 6.92 per cent. H.

Nitrogen.—0.4230 gram dried substance gave 63 cc. N at 13° C. (barometer 773 mm. at 23° C.) = 17.83 per cent. N.

The filtrate from the precipitate produced by carbon dioxide in the preparation of the preceding substance (**22**) was diluted with an equal volume of water, further treated with carbon dioxide for about three hours and allowed to stand overnight. The resulting precipitate was filtered off and washed with water,

alcohol and ether. 5 grams of substance having the same properties as Preparations **21** and **22** were thus obtained. Analysis of this product gave the following results:

OAT PROTEID *derived from Sodium Carbonate Solution of the "Albuminate."—Preparation* **23**.

		Ash-free.
Carbon	52.16	52.35
Hydrogen	7.00	7.02
Nitrogen	17.68	17.73
Sulphur	0.73	0.73
Oxygen	..	22.17
Ash	0.36	..
		100.00

Ash.—0.5500 gram substance, dried at 110° C., gave 0.0020 gram ash = 0.36 per cent.

Carbon and hydrogen.—0.4388 gram dried substance gave 0.8393 gram CO_2 = 52.16 per cent. C, and 0.2766 gram H_2O = 7.00 per cent. H.

Nitrogen.—0.3659 gram dried substance gave 54.36 cc. N at 13° C. (barometer 767.6 mm. at 22° C.) = 17.68 per cent. N.

Sulphur.—0.9135 gram dried substance gave 0.0484 gram $BaSO_4$ = 0.0066 gram S = 0.73 per cent. S.

Crystallisation of the Globulin obtained from the so-called "Albuminate."

300 cc. of 1-per cent. sodium chloride solution were heated to 70° C. with 5 grams, *i. e.* an excess of Preparation **21**, and filtered on a steam-jacketed funnel. On cooling, the filtrate rapidly deposited a large crop of rhombohedral crystals. The residue undissolved by the hot 1-per cent. brine was washed with the same weak brine heated to 70°. On cooling, the washings deposited octahedral crystals. This process was repeated several times with other portions of Preparation **21**. In most cases the filtrate deposited rhombohedral and the washings octahedral crystals. The residues which had been filtered out were, as far as possible, dissolved and crystallised from 1-per cent. brine, yielding either octahedral crystals or mixtures of octahedra and rhombohedra. The different crops of crystals were collected on separate filters, according as they were wholly rhombohedra or octahedra or mixtures of the two. Three preparations, "**24**," "**25**" and "**26**," were obtained in this way, and these were as

usual washed with water, alcohol and ether, and dried at 110° for analysis. Thus prepared they retained their crystalline form entirely unchanged, and had in all respects the same properties as the mother-substance (**21**).

Prof. S. L. Penfield kindly examined these crystals, and states that they appear to be rhombohedra and octahedra, athough the former have no action on polarised light. He suggests that the apparent rhombohedra may be octahedra with but six faces developed, such crystals occurring in nature. As they are too small for measurement (less than $\frac{1}{10}$ mm. long), this point cannot be definitely determined. Analyses of the three preparations gave the following percentages:

CRYSTALLISED OAT GLOBULIN *derived from* **21**.
Preparation **24**.

		Ash-free.
Carbon	52.14	52.17
Hydrogen	6.96	6.96
Nitrogen	17.92	17.93
Sulphur	0.53	0.53
Oxygen	..	22.41
Ash	0.06	..
		100.00

Ash.—0.4600 gram substance, dried at 110° C., gave 0.0003 gram ash = 0.06 per cent.

Carbon and hydrogen.—0.4463 gram dried substance gave 0.8835 gram CO_2 = 52.14 per cent. C, and 0.2795 gram H_2O = 6.96 per cent. H.

Nitrogen.—0.4042 gram dried substance gave 63.0 cc. N at 17° C. (barometer 756.3 mm. at 21° C.) = 17.92 per cent. N.

Sulphur.—0.6345 gram dried substance gave 0.0242 gram $BaSO_4$ = 0.0033 gram S = 0.53 per cent.

CRYSTALLISED OAT GLOBULIN *derived from* **21**.
Preparation **25**.

		Ash-free.
Carbon	52.00	52.11
Hydrogen	7.09	7.10
Nitrogen	17.91	17.94
Sulphur } Oxygen }	..	22.85
Ash	0.20	..
		100.00

Ash.—0.2035 gram substance, dried at 110°, gave 0.0004 gram ash = 0.20 per cent.

Carbon and hydrogen.—0.2562 gram dried substance gave 0.4885 gram CO_2 = 52.00 per cent. C, and 0.1635 gram H_2O = 7.09 per cent. H.

Nitrogen.—0.3935 gram dried substance gave 61.3 cc. N at 17° C., (barometer 756.5 mm. at 21° C.), = 17.91 per cent. N.

CRYSTALLISED OAT GLOBULIN *derived from* **21**. *Preparation* **26**.

		Ash-free.
Carbon	52.23	52.25
Hydrogen	7.08	7.08
Nitrogen	17.81	17.82
Sulphur	0.52	0.52
Oxygen	..	22.33
Ash	0.05	..
		100.00

Ash.—0.3974 gram substance, dried at 110° C., gave 0.0002 gram ash = 0.05 per cent.

Carbon and hydrogen.—0.2866 gram dried substance gave 0.5489 gram CO_2 = 52.23 per cent. C, and 0.1828 gram H_2O = 7.08 per cent. H.

Nitrogen.—0.3123 gram dried substance gave 48.31 cc. N at 17° C. (barometer 757 mm. at 21° C.) = 17.82 per cent. N.

Sulphur.—0.3598 gram dried substance gave 0.0135 gram $BaSO_4$ = 0.0018 gram S = 0.52 per cent.

CRYSTALLISED OAT GLOBULIN *derived from* **21**.

	24.—Rhombohedra.	**25**.—Rhombohedra- and Octahedra.	**26**.—Octahedra.
Carbon	52.17	52.11	52.25
Hydrogen	6.96	7.10	7.08
Nitrogen	17.93	17.94	17.82
Sulphur	0.53	22.85	0.52
Oxygen	22.41		22.33
	100.00	100.00	100.00
Ash	0.06	0.20	0.05

No chlorine could be detected in these crystals. It is thus shown that the crystallised globulin, except for its slightly lower content of sulphur, has the same composition as the mother-substance, and agrees in all respects with the globulin obtained directly from ground oats by extraction with hot salt-solution and described in my former paper, except that it is not soluble in water and contains a little less sulphur.

It is further to be noted that the methods of preparation rendered possible the fractional separation of the substance into its component parts, had it been a mixture of two or more globulins. It seems improbable that the sodium chloride which Grübler found in his crystallised globulin from squash-seed was anything more than an accidental impurity. The ash of Grübler's preparations contained traces of the various salts present in the solutions from which they separated, and there appears to be no good ground for Grübler's assumption that the crystallised proteids are definite compounds of globulin with sodium chloride or with other inorganic bodies, since the content of total mineral matters is variable and, as in my preparations **24** and **26**, sometimes amounts to but 0.05 per cent. of the proteid.

Globulin obtained by Direct Extraction of Ground Oats with Sodium Carbonate Solution.

100 grams of ground oats were digested with a 1-per cent. sodium carbonate solution, the extract was filtered clear, and the sodium carbonate converted into bicarbonate by treatment with carbon dioxide. The solution was then saturated with ammonium sulphate and the heavy precipitate filtered off. This precipitate was washed with a saturated solution of ammonium sulphate until the washings no longer reacted alkaline. The precipitate was then thoroughly extracted with salt solution and this extract dialysed. After the removal of the salts by dialysis, the proteid which had separated was filtered off and washed with alcohol and ether. It weighed, air-dry, 1.5 grams, being therefore about 1.5 per cent. of the oat kernel. Dried at 110° for analysis, it was found to have the following composition:

OAT PROTEID *extracted from Ground Oats by Sodium Carbonate Solution, and Soluble in Sodium Chloride Solution. Preparation* **27**.

			Ash-free.	
	I.	II.	I.	II.
Carbon	51.68	..	51.82	..
Hydrogen	6.91	..	6.93	..
Nitrogen	17.92	17.91	17.95	17.94
Sulphur } Oxygen }	..	..	23.30	..
Ash	0.26	..	..	..
			100.00	

Ash.—0.2652 gram substance, dried at 110° C., gave 0.0007 gram ash = 0.26 per cent.

Carbon and hydrogen.—0.2296 gram dried substance gave 0.4350 gram CO_2 = 51.68 per cent. C, and 0.1429 gram H_2O = 6.91 per cent. H.

Nitrogen, I.—0.3441 gram dried substance gave 52.15 cc. N at 13° C. (barometer 764.0 mm. at 25° C.) = 17.92 per cent. N.

Nitrogen, II.—0.3294 gram dried substance gave 50.14 cc. N at 14° C. (barometer 762.0 mm. at 23° C.) = 17.91 per cent. N.

Summary of Analyses of Oat Globulin.

The agreement of the analyses of the eight different preparations of oat globulin may be seen from the following table:

	20.	**21.**	**22.**	**23.**
Carbon	52.22	52.30	52 05	52.35
Hydrogen	6.98	6.98	6.93	7.02
Nitrogen	17.82	17.86	17.85	17.73
Sulphur	0.77	0.69	23.17	0.73
Oxygen	22.22	22.17		22.17
	100.00	100.00	100.00	100.00
	24.	**25.**	**26.**	**27.**
Carbon	52.17	52.11	52.25	51.82
Hydrogen	6.96	7.10	7.08	6.93
Nitrogen	17.93	17.94	17.82	17.95
Sulphur	0.53	22.85	0.52	23.30
Oxygen	22.41		22.33	
	100.00	100.00	100.00	100.00

The writer has nowhere found any description of a vegetable proteid like this. Although its proportion of carbon is the same as that of the globulin extracted from oats by cold salt-solution, its nitrogen-content is 1 per cent. greater. It contains nearly 1 per cent. less of nitrogen, about ½ per cent. more of carbon, and but ½ as much sulphur, as Chittenden and Hartwell[1] found in the globulin or "vegetable vitellin" of squash-seed.

Barbieri's analysis of squash-seed globulin agrees fairly well with these analyses of the crystallised oat globulin, but carbon and sulphur are somewhat lower, nitrogen high, and as regards sulphur and nitrogen his analysis differs materially from the later ones of Chittenden and Hartwell.

Grübler's earlier analyses of squash-seed globulin, which gave 53.21 per cent. of carbon and 19.22 per cent. of nitrogen, were

[1] J. Physiol **11**, 437–410.

evidently incorrect, and in a recent publication[1] this chemist states the composition of crystallised proteid from squash-seed as given below, where the various analyses of vegetable globulin, except this earlier one of Grübler's, are tabulated.

I have obtained from flax-seed a crystallised globulin whose composition agrees quite nearly with that of squash-seed vitellin.

Composition of Vegetable Globulin.

	Ritthausen.		Barbieri.	Ritth.	Chittenden and Hartwell.			Grübler.	Osborne.	
	Hemp.	Castor Bean.	Squash-seed.						Flax Seed.	Oats.
	Cryst.	Cryst.	Amorph	Cryst.	Cryst.	Spheroid	Amorph.	Cryst.	Cryst.	Cryst.
C	50.98	50.88	51.88	51.61	51.60	52.03	51.81	51.48	51.41	52.18
H	6.92	6.98	7.51	7.00	6.97	6.93	6.94	6.76	6.96	7.05
N	18.73	18.58	18.08	..	18.80	19.08	18.71	18.14	18.58	17.90
S	0.82	0.77	0.60	..	1.01	1.04	1.01	0.96	0.79	0.53
O	22.55	22.79	21.03	..	21.62	20.92	21.53	22.66	22.26	22.34
	100.00	100.00	100.00		100.00	100.00	100.00	100.00	100.00	100.00
Ash			1.11		0.30	0.36		0.18		0.10

Proteid extracted from Ground Oats by Direct Treatment with Alkali Carbonates.

The precipitate produced by saturating with ammonium sulphate the sodium carbonate extract of the oats from which the globulin **27** had been separated, was next washed with warm 80-per cent. alcohol until all the proteid soluble in that liquid was removed. The residue was then found to be quite insoluble in 1-per cent. sodium carbonate solution and was therefore treated with $\frac{2}{10}$-per cent. caustic potash solution, filtered, and the dissolved proteid completely precipitated by neutralising with dilute acetic acid. After washing this substance with water, alcohol and ether, and drying at 110°, its composition was as follows:

OAT PROTEID *extracted from Ground Oats by Sodium Carbonate Solution.—Preparation* **28**.

	I.	II.	Ash-free. I.	Ash-free. II.
Carbon	53.25	..	53.63	..
Hydrogen	7.13	..	7.18	..
Nitrogen	15.99	15.89	16.11	16.01
Sulphur	0.81	..	0.82	..
Oxygen	..	..	22.26	..
Ash	0.72	..	..	..
			100.00	

[1] J. prakt. Chem. **44**, 369.

Ash.—0.5661 gram substance, dried at 110° C., gave 0.0041 gram ash = 0.72 per cent.

Carbon and hydrogen.—0.3269 gram dried substance gave 0.6383 gram CO_2 = 53.25 per cent. C, and 0.2096 gram H_2O = 7.13 per cent. H.

Nitrogen, I.—0.3637 gram dried substance gave 49.33 cc. N at 13° C. (barometer 761.5 mm. at 25° C.) = 15.99 per cent. N.

Nitrogen, II.—0.3916 gram dried substance gave 52.95 cc. N at 13° C. (barometer 759.2 mm. at 23° C.) = 15.89 per cent. N.

Sulphur.—0.5000 gram dried substance gave 0.0295 gram $BaSO_4$ = 0.0041 gram S = 0.81 per cent. S.

If this analysis is compared with that of Preparation **17**, which was obtained from ground oats by direct extraction with $\frac{2}{10}$-per cent. potash solution, it will be seen that the two agree closely.

	28.	**17.**
Carbon	53.63	53.49
Hydrogen	7.18	7.01
Nitrogen	16.11	16.39
Sulphur	0.81	0.99
Oxygen	22.27	22.12
	100.00	100.00
Ash	0.72	1.00

These two bodies are thus shown to be essentially the same in composition, and the results of direct extraction with alkili as given in my first paper are confirmed.

Conclusion.

The proteids of the oat kernel undergo great change in contact with water or sodium chloride solution. The body extracted by direct treatment of ground oats with alcohol differs much in properties and composition from that extracted by alcohol after the ground oats have for some time had contact with water or sodium chloride solution.

Direct treatment with sodium carbonate solution yields the same globulin as that obtained by direct treatment with hot sodium chloride solution, but differing from that obtained by direct treatment with cold sodium chloride solution. Sodium carbonate solution also extracts another proteid—the same as that yielded by direct extraction with dilute potash-lye—which, again, is distinct in composition from that obtained after the oats have been in contact with water. It is remarkable that all these transformations are the result of the use of water or salt-solution

as contrasted with the use of alcohol, alkali or heat: three agents known to suspend or destroy ferment action.

The fact that the globulin extracted after treatment of the ground oats with alcohol has the same composition as that obtained by direct treatment with sodium chloride, would indicate that alcohol temporarily suspends a ferment-action which is induced by water or solutions of neutral salts.

It is probable that the primary proteids originally contained in the oat kernel are the three following bodies:

PRIMARY OAT PROTEIDS.

	Alcohol-soluble Proteid— Average of five analyses.	Salt-soluble Proteid or Globulin— Average of nine analyses.	Alkali-soluble Proteid— Average of two analyses.
Carbon	53.01	52.19	53.56
Hydrogen	6.91	7.00	7.09
Nitrogen	16.43	17.86	16.20
Sulphur	2.26	0.65	0.90
Oxygen	21.39	22.30	22.25
	100.00	100.00	100.00

Of the above substances the alcohol-soluble proteid forms about 1.25 per cent., the globulin about 1.5 per cent., and the alkali-soluble body the remainder of the proteids contained in the oat kernel, with the possible exception of extremely small amounts of proteose and acid-albumin. The latter two substances are quite probably the results of change occurring during extraction; the evidence, however, on this point is not conclusive.

Three other proteids are obtained—evidently by the alteration of the primary proteids, and probably through ferment-action—if the ground oats are subjected to contact with water or solutions of neutral salts. The composition of these derived or secondary proteids is as follows:

SECONDARY OAT PROTEIDS.

	Alcohol-soluble Proteid— Average of four analyses.	Salt-soluble Proteid or Globulin— Average of four analyses.	Alkali-soluble Proteid— Average of two analyses.
Carbon	53.70	52.34	52.49
Hydrogen	7.00	7.21	7.10
Nitrogen	15.71	16.88	17.11
Sulphur	1.78	0.88	0.80
Oxygen	21.83	22.69	22.50
	100.00	100.00	100.00

It would appear that none of the proteids from the oat kernel have hitherto been obtained and analysed in a state of purity. The author therefore reserves the right to revise the nomenclature of these bodies after further progress in his researches on the other vegetable proteids with which he is now engaged.

LABORATORY OF THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION, NEW HAVEN, CONN., *November*, 1891.

EUPATORIN: THE ACTIVE PRINCIPLE OF *EUPATORIUM PERFOLIATUM.*

BY C. H. SHAMEL.

The dried *eupatorium perfoliatum*, gathered at blooming-time, was extracted by hot alcohol in a continuous extraction-apparatus for several hours. The excess of alcohol was distilled off and the thick residue treated with water acidulated with hydrochloric acid. A black gummy mass separated, which was removed by filtration, the filtrate neutralised with sodium carbonate and extracted with ether. On evaporation of the ether the active principle was deposited, either as a yellow resinous mass or as a yellow powder, which, on examination under the microscope, was found to consist of globular masses of needle-shaped crystals. The crystalline variety was analysed for nitrogen, but was found to contain none. The principle, in both the amorphous and crystalline forms, was insoluble in water, in concentrated sulphuric acid and in concentrated hydrochloric acid, but was soluble in even dilute nitric acid with a light-brown coloration. The nitric-acid solution, when allowed to evaporate spontaneously or in a vacuum over lime, crystallises in beautiful prisms and six-sided plates.

An aqueous solution of these crystals injected into mice killed them in a few hours. The crystals, when taken into the mouth, have first an acid taste from the nitric acid they contain, followed by a very bitter taste. The aqueous solution has only the bitter taste.

Chemical Characteristics.

The crystals of the nitrate are easily soluble in water and melt at 102°–103°. The principle itself does not melt, but at 250° suffers partial decomposition.

The solution of the nitrate was tested with the common alkaloid reagents, but gave the following reactions only: Phospho-molybdic acid, a green color; picric acid, a few needle-shaped crystals; auric chloride, colored slightly.

The principle is soluble in the alkalies. The solution in sodium hydroxide gave the following reactions, parallel tests being made with the sodium hydroxide solution alone: Phospho-molybdic acid, an instantaneous brilliant green coloration which soon fades; auric chloride, a black flocculent precipitate; picric acid, a deep-red coloration.

The ultimate analysis of the crystallised nitrate deprived of its water of crystallisation gave the following figures:

C	H	O	N
25.7 per cent.	3.1 per cent.	64.2 per cent.	1.55 per cent.
26.2	2.7	64.1	1.6

Or calculating the N as HNO_3, we have HNO_3 { 6.97 per cent. / 7.20

These figures would indicate that the formula is $C_{20}H_{28}O_{26}.HNO_3$, which would require the following as the theoretical composition:

C—26.49 per cent. H—2.76 per cent. O—64 per cent.
N—1.54 per cent. = HNO_3—6.96 per cent.

DI-BENZYLCARBINAMINE AND ITS CONDUCT TOWARD NITROUS ACID.

By W. A. Noyes.

Some time since Bamberger discovered several representatives of a new class of amines, to which he has given the name of "alicyclic."[1] The structural characteristic of this class of bases

[1] Ber. d. chem. Ges. **22**, 769.

is that the amine group is combined with a carbon atom which forms a part of a hydrogenated benzene nucleus. Those prepared by Bamberger have been derivatives of naphthalin.[1] Bornyl amine[2] and hexamethylene diamine[3] show similar properties. It is probable that the menthyl amine recently prepared by Wallach[4] will show a similar conduct, but a full description of the body has not been published.

As regards their chemical character, the alicyclic amines are strong bases; their carbonates are precipitated from ethereal solutions of the bases by moist carbon dioxide, are stable salts, and have a strongly alkaline reaction; the free bases combine directly with carbon disulphide at ordinary temperatures, forming sulphocarbamates; and the nitrites are stable and do not decompose even in boiling water. In this last respect, especially, the alicyclic amines differ from all other amines at present known.

The conduct of these amines suggests the question whether their peculiar behavior is characteristic only of alicyclic bases, or whether possibly other amines might be found which would show similar properties. The facts that naphthobenzyl amine forms a nitrite which is stable at low temperatures,[5] and that di-iso-propylamine forms a nitrite which is converted into a nitroso compound only by long boiling with water,[6] indicate that aliphatic bases may, in some cases, be comparatively stable toward nitrous acid. It seemed possible that a base containing the amine group connected with the central carbon atom in a somewhat large carbon complex, might show a similar conduct to that of an amine group connected with a hydrogenated benzene nucleus. In order to test this question, di-benzylcarbinamine has been prepared and its character studied.

The base was obtained by the reduction of di-benzylketoxim by means of sodium and absolute alcohol. A hot solution of 13.5 grams of the ketoxim in 100 cc. of absolute alcohol was poured slowly into a flask connected with an inverted condenser and containing 20 grams of sodium. When the reaction slackened the flask was heated with a low flame, and alcohol was added in portions of 25 cc. at a time whenever a crust of sodium ethylate appeared on the sodium. When the sodium had disappeared,

[1] Ber. d. chem. Ges. **20**, 2915; **21**, 847, 1112, 1786, 1892; **22**, 625, 767, 777, 943, 1295, 1311, 1374, 1760; **23**, 291, 876.
[2] Ibid. **21**, 1126. [3] Ibid. **22**, 2172. [4] Ibid. **24**, 3992.
[5] Ibid. **21**, 257.
[6] Rec. trav. Chim. **8**, 207. See also Ber. d. chem. Ges. **22**, Ref. 343.

the alcohol and a part of the base were distilled in a current of steam. It was found, however, that the base is very difficultly volatile even with superheated steam, and also that some of the unchanged oxim passed over, so that the pure base could not be separated by this method. The following method was found more satisfactory After distilling off the alcohol with a current of steam the alkaline solution was diluted slightly and allowed to cool. The base is almost insoluble in water and separates, together with some unchanged oxim, as an oily liquid. The liquid was separated from the alkaline solution by filtration or by means of a little ether, and the base was converted into the chloride by treatment with dilute hydrochloric acid. The solution was then rendered slightly alkaline with caustic soda, and then acid with acetic acid. After standing for some time the oxim separates almost completely, and can be removed from the solution by filtration. Caustic soda will then precipitate the base from the filtrate in a nearly pure condition. It can be further purified by conversion into the chloride and recrystallisation of the salt from water.

Di-benzylcarbinamine.

The free base separates in oily drops when caustic soda is added to a solution of one of its salts. After some time the drops solidify to a crystalline mass, a transformation which can be much hastened by the addition of some small particles of the solid base.

After drying over sulphuric acid the base melts at 47° and boils without decomposition at 330°. The base dissolves readily in alcohol, ether and ligroin, but is nearly insoluble in water. It is not hygroscopic. It shows a strongly alkaline reaction with test papers. The analyses gave the following results:

I. 0.1874 gram of the base gave 0.5851 gram CO_2 and 0.1328 gram H_2O.

II. 0.2198 gram of the base gave 0.6854 gram CO_2 and 0.1589 gram H_2O.

	Calculated for $\begin{matrix}C_6H_5CH_2\\C_6H_5CH_2\end{matrix}>CHNH_2$.	Found. I.	II.
C_{15}	85.31	85.17	85.05
H_{17}	8.06	7.87	8.03
N	6.63	...	...

The chloride, $C_{15}H_{15}NH_2HCl$, separates in compact crystals, which group themselves in warty aggregates on the bottom of the

crystallising dish. The salt is moderately soluble in water. It melts sharply at 205°.

0.1936 gram of the salt gave 0.1113 gram of AgCl.

	Calculated.	Found.
Cl	14.34	14.22

The chloroplatinate, $(C_{15}H_{15}NH_3)_2PtCl_6$, is precipitated in fine crystalline scales having a light-yellow color when chloroplatinic acid is added to a solution of the chloride of the base. The salt may be recrystallised from hot water without decomposition.

0.2215 gram of the salt gave 0.0514 gram Pt.

	Calculated.	Found.
Pt	23.44	23.21

The nitrite, $C_{15}H_{15}NH_2HNO_2$, is precipitated in fine needles which form a compact, cotton-like mass when a solution of sodium or potassium nitrite is added to a concentrated solution of the chloride. After filtering off and drying over sulphuric acid, a weighed portion of the salt was dissolved in water and a known part of the very dilute solution was treated with hydrochloric acid, sulphanilic acid and naphthylamine chloride. A standard solution of sodium nitrite containing the amount of nitrous acid calculated to correspond to the solution containing the nitrite of the base was treated with the same reagents, and the colors were compared. No difference could be detected in the tints.

At ordinary temperatures solutions of the nitrite appear to be perfectly stable, and there is no difficulty in obtaining the salt in pure condition. Dilute solutions may be boiled for some time with very slight decomposition, as was proved by quantitative color reactions. When, however, a concentrated solution of the nitrite is heated to the boiling point, nitrogen is evolved and di-benzyl carbinol is formed as the chief product of the decomposition. The details are given below.

Di-benzylcarbinamine sulphocarbamate of di-benzylcarbinamine, $\begin{matrix} C_{15}H_{15}NH \\ C_{15}H_{15}NH_2HS \end{matrix}\!\!>\!CS$, is formed when di-benzylcarbinamine is added to carbon di-sulphide. The base dissolves completely at first, but in a moment the salt begins to separate and soon fills the liquid with an almost solid mass of very fine crystals. These were filtered off, washed with carbon disulphide and allowed to dry in the air. The substance melts at 141°–143°. At the same time it decomposes and hydrogen sulphide is evolved,

probably with the formation of a thio-urea, $\begin{matrix}C_{15}H_{15}NH\\C_{15}H_{15}NH\end{matrix}>CS$. The analysis of the salt gave the following result:

0.0924 gram of the substance gave 0.0870 gram $BaSO_4$ (Carius).

	Calculated for $\begin{matrix}C_{15}H_{15}NH\\C_{15}H_{15}NH_2HS\end{matrix}>CS$.	Found.
S	12.85	12.94

Di-benzylcarbinol.

To obtain the substance formed by the decomposition of the nitrite of di-benzylcarbinamine, 5.8 grams of the chloride of the base were dissolved in about 30 cc. of water, and a strong solution of sodium nitrite containing 1.62 grams of the salt was added. The solution was then heated overnight on the water-bath. The product of the decomposition which separated as an oil, heavier than water, was taken up with a small amount of ether; the ethereal solution was dried with potassium carbonate and was then distilled. The product distilled mainly at 320°–325°. The analysis of a portion of the distillate indicated that it consisted of a mixture of di-benzylcarbinol and of the hydrocarbon which would be obtained from the alcohol by the loss of one molecule of water.

0.2754 gram of the liquid gave 0.8830 gram CO_2 and 0.1844 gram H_2O.

	Calculated for $\begin{matrix}C_6H_5CH_2\\C_6H_5CH_2\end{matrix}>CHOH$.	Found.	Calculated for $\begin{matrix}C_6H_5CH\\C_6H_5CH\end{matrix}\!\!\rangle CH$.
C	84.90	87.48	92.78
H	7.55	7.44	7.22

Thinking that decomposition might have taken place during the distillation, a fresh solution of the chloride of the base was taken, the equivalent amount of sodium nitrite was added, and the solution was heated for a short time on the water-bath. The oil which separated was washed with water and dried over sulphuric acid in a vacuum. Two different specimens of the alcohol prepared in this way were analysed. The specimen used for the second and third analyses was heated on the water-bath for a shorter time than that used for the first analysis. The results of the analyses indicate that di-benzylcarbinol is the chief product of the decomposition of the nitrite, but that a small amount of some substance richer in carbon, probably an unsaturated hydrocarbon, is formed.

I. 0.1283 gram of the oil gave 0.4020 gram CO_2 and 0.0841 gram H_2O.

II. 0.1756 gram gave 0.5511 gram CO_2 and 0.1180 gram H_2O.

III. 0.1336 gram gave 0.4188 gram CO_2 and 0.0752 gram H_2O.

	Calculated for $C_6H_5CH_2$ / $C_6H_5CH_2$ >CHOH.	Found. I.	II.	III.
C	84.90	86.08	85.59	85.49
H	7.55	7.28	7.47	7.52

Di-benzylcarbinol, when prepared as described, is a viscous liquid, heavier than water and having a slight yellow color, probably due to impurities. The boiling point is probably between 320° and 325°, but the determination cannot be considered as accurate. Freund and Shönfeld[1] have recently shown that the nitrite of a nonyl-amine gives by its decomposition a tertiary alcohol, instead of the primary alcohol which would be expected. To determine whether a similar change had taken place in the present case, a small quantity of the di-benzylcarbinol was dissolved in glacial acetic acid, and an excess of a cold solution of chromic acid in acetic acid was added. After standing for a few minutes the solution was diluted with water, and the oil which separated was taken up with ether. The ethereal solution was shaken with caustic soda to remove acetic acid and then evaporated to dryness. The oily residue was dissolved in alcohol, hydroxylamine chloride and caustic soda were added, and the solution was heated on the water-bath for half an hour. The oxim which was precipitated on pouring the solution into water was dried over sulphuric acid and recrystallised from ligroin. It separated in short white needles, identical in appearance with those of the oxim of di-benzylketone, and melting at the same temperature, 121°. Rattner[2] gives the melting point as 119.5°. The substance formed by the decomposition of di-benzylcarbinamine nitrite is, therefore, di-benzylcarbinol and not an isomer.

It appears from the experiments which have been described that the nitrite of di-benzylcarbinamine is more stable than the nitrites of most aliphatic amines. It does not, however, have the same stability as the nitrites of the "alicyclic" amines, and the latter form a class distinct in their properties from all other amines at present known.

Rose Polytechnic Institute, *March*, 1892.

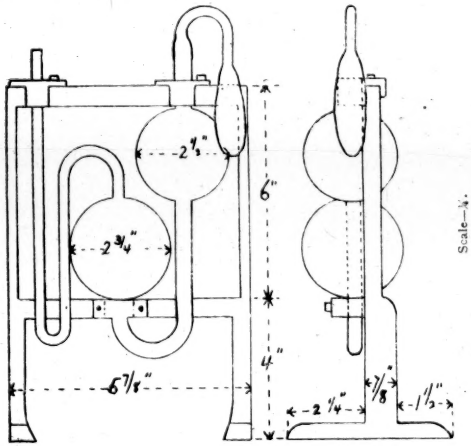
[1] Ber. d. chem. Ges. **24**, 3359.

[2] Ibid. **21**, 1317.

AN IMPROVED PIPETTE FOR GAS ABSORPTIONS.[1]

By Augustus H. Gill.

The writer has replaced the cumbersome "compound" pipette of Hempel by the "simple" one, fitted with a rubber bag after the manner of the pipettes in the Orsat gas apparatus, as furnished by Muencke. This has been found to preserve the reagents better and to possess the additional advantage of being much more easily refilled and handled.



The capillary is made of "white laid" glass, similar to that used for thermometers, and does away with the milk-glass tablet which is usually inlaid behind this part. To prevent the rubber connectors from slipping off, the end of the capillary is ground rough. A cast-iron stand is the mounting of the pipette, its tubes passing through movable brass pieces, and being held fast by filling in the annular space with a molten mixture of equal parts of rosin and beeswax[1]; rubber tubing or cork can also be used for this filling. These stands admit of almost any size of pipette being used and of its easy replacement in case of breakage.

The apparatus was made for me most satisfactorily by Mr. Albert Hetschel, 33 Woodville Street, Boston.

Laboratory of Gas Analysis, Mass. Institute of Technology, Boston.

[1] The apparatus can be obtained from Emil Greiner, New York.

Contributions from the Chemical Laboratory of Cornell University.

XVIII.—ON THE COPPER SULPHITES.

By Spencer B. Newbury.

In the course of an extended investigation of the compounds of copper and silver—undertaken in the hope of throwing some light on the peculiar differences which these two elements present, though belonging to the same family in the periodic system—the author's attention was called to the peculiar action of sulphur dioxide upon copper salts, and a series of experiments were made which have yielded interesting results, though somewhat aside from the purpose of the original investigation.

Cupric sulphite appears never to have been prepared. According to Musspratt,[1] cupric hydroxide is dissolved by a solution of sulphur dioxide to a green liquid which perhaps contains cupric sulphite; on standing or warming, a red crystalline salt is precipitated; this was supposed to be cuprous sulphite, but Rammelsberg proved it to be a cuproso-cupric sulphite, $CuSO_3.Cu_2SO_3.2H_2O$. By the action of sulphur dioxide on a mixed solution of cupric sulphate and ammonium sulphite, white leaflets of ammonium-cuprous sulphite were obtained by Rogojski and others, and by further action of sulphur dioxide this substance is converted into cuprous sulphite, $Cu_2SO_3.H_2O$. This compound forms red crystals, and closely resembles the cuproso-cuprous sulphite mentioned above. By the action of sulphur dioxide on a solution of cupric acetate, Etard[2] obtained cuprous sulphite in another form, *i. e.* in white crystalline leaflets; the red sulphite obtained by Rogojski is claimed by Etard to be a polymeric form of the same substance.

Action of sulphur dioxide on copper sulphate in presence of copper.—The formation of the cuproso-cupric sulphite by the action of sulphur dioxide on cupric hydroxide is evidently due to partial reduction of the cupric sulphite first formed:

$$3CuSO_3 + SO_2 + H_2O = CuSO_3.Cu_2SO_3 + H_2SO_4.$$

It appeared probable to the author that, if the above constitution of this salt is correct, it should be formed by the action of sulphur

[1] Ann. Chem. (Liebig) **50**, 284. [2] Compt. rend. **95**, 36, 137.

dioxide on copper sulphate solution in presence of metallic copper. This was found to be the case. A roll of thin sheet copper was placed in a ten-per cent. solution of copper sulphate, and a slow current of sulphur dioxide passed in for several hours. The copper soon became covered with a coating of red crystals, and the solution became at last almost completely decolorised. The crystals showed the characteristic form of the red salt. A determination of copper gave the following result:

	Calculated for $CuSO_3.Cu_2SO_3.2H_2O$.	Found.	
Cu	49.25	49.40	49.26

The loss of weight of the copper used was found to be about one-third of the copper contained in the salt: wt. of salt, 5.5676 grams; loss in wt. of copper, 1.0616 grams. From this it would appear that cupric sulphite is formed by the action of the sulphur dioxide on the copper sulphate, and that this is converted by the copper into cuproso-cupric sulphite: $2CuSO_3 + Cu = CuSO_4.Cu_2SO_3$. As the latter is constantly removed from the solution, the action of the sulphur dioxide continues until the decomposition of the sulphate is nearly complete. A large amount of sulphuric acid is, however, produced in the solution, and this brings about finally a condition of equilibrium beyond which point the action of the sulphur dioxide ceases.

Action of sulphur dioxide on cupric hydroxide.—It appeared to the author to be of interest to determine whether, in dissolving cupric hydroxide in sulphur dioxide solution, the reduction to the red salt takes place at once, or whether the solution actually contains cupric sulphite, which is reduced only on standing or heating.

Moist cupric hydroxide, previously washed until free from sulphate, was placed in a beaker surrounded by ice-water, and sulphur dioxide passed in until the solution was complete. The blue hydroxide is first converted into a yellowish substance; this gradually dissolves to a dark-green solution. In the cold this solution may be preserved for a considerable time without change, but on standing for a few hours, or immediately on warming, it throws down a heavy crystalline deposit of the red salt, while the solution becomes nearly colorless.

In order to determine whether the reduction to the red salt had already taken place in the green solution, the amount of sulphuric

acid present in a given volume was determined, while an equal volume was heated to boiling, and the sulphuric acid contained in it was determined after the separation of the red salt. In the first case this could not be done by acidification and precipitation with barium chloride, since by this process cupric chloride is formed, and is immediately reduced by the sulphur dioxide present with formation of sulphuric acid. The green solution was therefore carefully precipitated by barium hydroxide, and the resulting mixed precipitate of sulphite and sulphate exhausted on the filter with hot hydrochloric acid.[1] One experiment gave the following result:

Before boiling, the green solution gave 0.0520 $BaSO_4$.

After boiling, an equal volume gave 0.3404 $BaSO_4$.

In this case a very slight separation of the red salt had already taken place before the determination. With care, keeping the material quite cold, it is possible to obtain a solution of cupric hydroxide in sulphurous acid, which is free from sulphuric acid. These experiments show that no reduction to cuprous compounds takes place in dissolving cupric hydroxide in sulphur dioxide solution, and that in the green solution all the copper present is in the cupric condition.

All attempts to obtain a crystalline cupric sulphite by evaporation of the solution were without result, as in every case a deposit of the red salt was soon formed.

It was noticed that, on exposure to the air, the green sulphurous-acid solution of cupric hydroxide becomes covered with a yellow film. On passing a current of air through the liquid, the solution first becomes nearly black, then gradually throws down a precipitate of a bright-yellow-ochre color. The same substance is obtained as a flocculent yellow precipitate on addition of alcohol to the solution. This compound dries in the air to a bright-yellow powder. It dissolves in dilute hydrochloric acid to a green solution, giving off sulphur dioxide, and without separation of cuprous chloride, and in dilute sulphuric acid without separation of metallic copper; this behavior shows it to be a cupric compound. From its character and mode of formation it appeared probable that the compound is a basic cupric sulphite. This view was fully confirmed by a study of the composition and reactions of the substance.

[1] This could also have been done by boiling the solution with sodium carbonate, and after filtering off the copper oxide separated, determining the sulphate in the solution of sodium salts.

Basic cupric sulphite.—This compound was prepared in considerable quantities in the following manner: Cupric hydroxide was precipitated in the presence of ammonium sulphate, and washed repeatedly by decantation through a cotton-cloth filter until free from sulphate. The cupric hydroxide was brought upon a cotton filter and freed from most of the water by suction; the stiff paste was placed in a beaker surrounded by water at 0°, and a rapid current of washed sulphur dioxide passed in until complete solution resulted. The green liquid was then poured into twice its volume of 90-per cent. alcohol, and the precipitate collected by suction on a filter. The wet precipitate was then repeatedly washed by agitating with water, and filtration, until the filtrate no longer showed the presence of soluble sulphates. The material is slightly soluble in water, communicating a green tint to the washings. This color disappears at once on the addition of a few drops of hydrochloric acid, showing that the sulphite has a much greater coloring power than the chloride. The precipitate was finally washed twice with alcohol, and allowed to dry spontaneously in the air. So prepared, it is an amorphous powder of bright yellow-ochre color. Dried at 100° in air, hydrogen or carbon dioxide, it loses some sulphur dioxide, and changes in color to grayish-brown. The substance was therefore analysed in the air-dry condition, and the results calculated for material dry at 100°. For this purpose it was necessary to determine the moisture present in the air-dry samples. This was accomplished by heating to 100°–110°, in a current of dry hydrogen or carbon dioxide; the sulphur dioxide given off on drying was estimated by passing the gas through bromine water, and subsequently determining the sulphuric acid formed, by means of barium chloride. The amount of sulphur dioxide given off on drying proved to be slight, but was sufficient to make it impossible to obtain absolutely constant weight. The determinations of copper were made by the battery in sulphuric-acid solution; those of sulphur by oxidation by boiling with bromine water and precipitation of the sulphur as barium sulphate. The substance being a copper compound, the method of titrating the sulphur dioxide by standard iodine solution could not be employed. The determination of water of constitution presented great difficulties, owing to the fact that it is given off together with much sulphur dioxide at about 160°. Owing to the liberation of sulphur dioxide, the

estimation of the water by direct weight gave rather variable results. The determinations were finally made by gently igniting the substance in a combustion-tube in a current of dry carbon dioxide, conducting the gas from the tube into bromine water and subsequently estimating the sulphuric acid formed in the latter. The loss of weight of the substance, *minus* the weight of the sulphur dioxide, was taken as the amount of combined water. These determinations are, however, not wholly satisfactory, as the material gradually loses some water and sulphur dioxide at all temperatures between 100° and 160°, and it is impossible to draw the line sharply between hygroscopic and combined water. At about 160°, however, the substance suddenly undergoes complete decomposition, contracting much in volume, and becoming reddish-brown in color.

A number of samples, separately prepared, were analysed, with results which show that the substance, though unstable, is of perfectly definite composition, and has the formula $3CuO.2SO_2$, with probably $1\frac{1}{2}$ molecules of water.

	Calculated for $3CuO.2SO_2.1\frac{1}{2}H_2O$.	Found. I.	II.		III.	IV.
Cu	48.38	48.68	48.46	48.39	48.60	48.65
S	16.28	15.87	15.86	15.83	16.39	16.23
O	28.48	...	...	...	...	...
H_2O	6.86	...	6.19	...	6.98	6.64

On boiling with water, the compound undergoes a complete decomposition, which strongly supports the above view of its constitution. On boiling for a few minutes, it gives a deep-blue solution of copper sulphate, and a brown insoluble substance, which is completely converted by hydrochloric acid into cuprous chloride with liberation of sulphur dioxide, and dissolves in sulphuric acid with separation of metallic copper. This substance thus appears to be cuprous sulphite, formed according to the reaction

$$3CuO.2SO_2 = CuSO_4 + Cu_2SO_3.$$

On continuing the boiling with water, sulphur dioxide is given off, and finally bright-red cuprous oxide remains, suspended in blue solution of cupric sulphate:

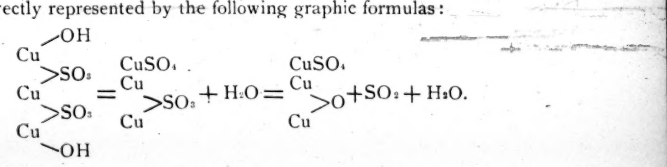
$$3CuO.2SO_2 = CuSO_4 + Cu_2O + SO_2.$$

If this equation be correct, one-third of the copper should appear as cupric sulphate, and two-thirds as cuprous oxide. A

quantitative experiment gave the following results: 0.5000 gram of air-dry substance (containing 13.18 per cent. moisture, and corresponding to 0.4341 gram dry substance) gave—

	Calculated.		Found.	
	In $CuSO_4$.	In Cu_2O.	In $CuSO_4$.	In Cu_2O.
Cu	0.0700	0.1400	0.0717	0.1407

If it is assumed that a portion of the water present exists in the form of cupric hydroxide, the above reactions may, perhaps, be correctly represented by the following graphic formulas:



The same transformation takes place also on heating the dry substance to 160°, since the residue, on treating with water, gives at once a blue solution of cupric sulphate.

The ready conversion of basic cupric sulphite into the red cuproso-cupric sulphite indicates that the two compounds are similarly constituted. Further experimental work is, however, necessary, in order to determine the precise relation between them. It appears probable that further study of the basic cupric sulphite, and of the cuproso-cupric sulphite and cuprous sulphite, into which it is so easily transformed, will, on account of the simple decompositions which these compounds undergo, throw important light on the structure of the sulphites.

When moist basic cupric sulphite is exposed to the air it is gradually oxidised, forming cupric sulphate, which may be dissolved out in water, leaving a yellowish-green insoluble powder which gives all the reactions of the original substance. It is probably a basic cupric sulphite of simpler constitution than the one described above, but further study is necessary to determine its exact nature.

In conclusion, attention may be called to the interesting relation which exists between the sulphites and carbonates of copper. As with sulphurous acid, copper forms with carbonic acid no neutral salts, the only cupric carbonates known being azurite, $3CuO.2CO_2.H_2O$, and malachite, $2CuO.CO_2.H_2O$. It will be seen that

the basic cupric sulphite, $3CuO.2SO_2.1\frac{1}{2}H_2O$, described in this paper, corresponds closely in its constitution with azurite. Cupric oxide is a weak base, and with weak acids, such as carbonic or sulphurous acids, it appears to be incapable of entering into combination in the proportion necessary to form neutral salts. The basic carbonates, like the basic sulphite, are decomposed on boiling with water, the carbonates giving off carbon dioxide and leaving cupric oxide. The difference in the two reactions

$$3CuO.2SO_2 = CuSO_4 + Cu_2O + SO_2$$
$$3CuO.2CO_2 = 3CuO + 2CO_2$$

is doubtless due to the capacity of sulphur to form a higher acid-forming oxide than SO_2, a power not possessed by carbon, and also, perhaps, to a fundamental difference in the structure of the sulphites and carbonates.

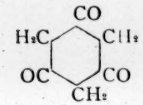
REVIEWS AND REPORTS.

TAUTOMERISM.

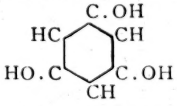
It has been known for some time that two different chemical substances could be represented correctly by the same structural formula. This peculiar kind of isomerism Wislicenus calls geometrical isomerism, and under the name of stereochemistry[1] there has been developed a theory to explain it by an extension of the Van't Hoff and Le Bel hypothesis of the space relation between the atoms or groups of atoms.

The opposite conception, that the constitution of the same chemical compound under different circumstances could be accurately represented by two totally different structural formulas, has now become quite general. Compounds which belong to this class seem to possess a double character, appearing in one reaction to have one constitution and in another to have an entirely different structure. Thus Von Baeyer[2] found that phloroglucin gave a trioxime with hydroxylamine, and was undoubtedly to be regarded as a ketone derived from hexamethylene, *i. e.* a 1, 3, 5 keto-hexamethylene:

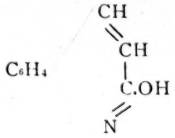
[1] This Journal **9**, 453. [2] Ber. d. chem. Ges. **19**, 159.



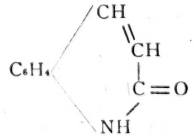
Its reactions in general, however, showed it to be plainly a trihydroxy-benzene having the following formula:



Other substances have been shown to exhibit a like conduct. Carbostyril, for example, yields, according to Friedländer,[1] two alkyl carbostyrils, $C_9H_6(OR)N$ and $C_9H_6O(NR)$, when treated with an alkali and an alkyl halogen. This would seem to indicate that carbostyril existed, or at least reacted, in two forms, the first having the formula



i. e. a lactim; and the second a lactam formula,



To explain this peculiar chemical conduct, Baeyer assumes the existence of pseudo or unstable forms. These pseudo forms are conceived as resulting from a change of position of the hydrogen atoms within the molecule, and may be determined by certain reactions. Thus phloroglucin is undoubtedly a trioxybenzene, and yet the reaction with hydroxylamine shows that it exists also in the form of a ketone. Hence 1, 3, 5 trioxybenzene is called phloroglucin, and the 1, 3, 5 keto-hexamethylene, pseudo-phloroglucin by Baeyer.

In 1885 C. Laar[2] published an article entitled "Ueber die Möglichkeit mehrerer Strukturformeln für dieselbe chemische

[1] Ber. d. chem. Ges. **18**, 1528; **20**, 2009. [2] Ibid. **18**, 648; see also **19**, 730.

Verbindung," in which he enumerates the most important compounds showing this peculiar conduct. To this phenomenon he gives the name of tautomerism (ταὐτό, the same, and μέρος, parts). Compounds like phloroglucin, carbostyril, etc., are called tautomeric. To explain tautomerism, Laar assumes that, according to the principle of changing combination within the molecule of a tautomeric body, a constant change of place of the easily mobile hydrogen atom occurs, so that the different arrangements of the hydrogen atoms corresponding to the structural formulas deduced are to be regarded merely as phases of an intramolecular motion. Thus to take the simplest case mentioned by him, viz. hydrocyanic acid. The chemical conduct of this substance may be represented by the two tautomeric formulas,

$$H-C\equiv N \text{ and } H-N=C.$$

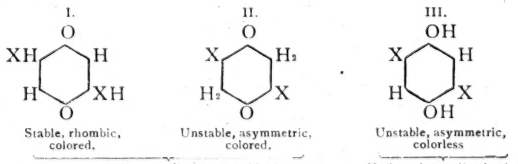
In the first of these formulas the hydrogen atom is represented as connected with the carbon atom; in the second with the nitrogen atom, and Laar conceives of the hydrogen atom as oscillating alternately between the one and the other position. Both forms must exist in solution together, therefore, according to Laar.

Most chemists, however, are inclined to agree with Baeyer[1] that the phenomenon designated by Laar as tautomerism is rather to be explained by assuming the existence of unstable atom groupings (pseudo forms) besides the stable groupings, *i. e.* the normal positions of equilibrium, and that therefore each of the molecular arrangements designated by Laar as tautomeric really possesses a definite constitution.

For the expression tautomerism made use of by Laar, the more exact designation desmotropism (δεσμός, bond, and τροπή, changing) has been suggested by P. Jacobson,[2] according to Victor Meyer. Hantzsch and Hermann[3] employ both these expressions, but they use each in a different sense. The characteristic property shown by certain compounds of reacting in different ways in typical reactions is to be designated according to them as tautomerism, while a body exhibiting such conduct could be called briefly tautomeric. Now this property of tautomerism depends upon the easy mobility of the hydrogen atoms within the molecule. As a designation, therefore, of the actual change of union taking place and the new distribution of the hydrogen atoms within the molecule of a tautomeric body thereby conditioned, the expression desmotropism alone is used. The arrangement of the atoms within this molecule, determined by the different conduct of a tautomeric compound, and distinguished by a different distribution of hydrogen atoms, may be called the desmotropic condition.

[1] Ber. d. chem. Ges. **16**, 2188. [2] Ibid. **20**, 1732, foot-note. [3] Ibid. **20**, 2801.

The structural formulas corresponding to the different desmotropic conditions bear the same relation to each other that the formulas of isomeric bodies do, but Hantzsch and Hermann hold that the characteristic distinction of desmotropism as opposed to isomerism is that under definite physical conditions only a single one of the desmotropic forms is stable, at least in the solid state. However, a tautomeric body under changed external conditions may assume another desmotropic form. This change will become known by the appearance of the body in question in another form having different physical properties. Thus succino-succinic ether and a number of its derivatives, according to Hantzsch and Hermann, are shown by their chemical conduct to be tautomeric. These react sometimes as quinones, sometimes as hydroquinones, *i. e.* in the sense of the desmotropic conditions distinguished by the atom grouping $-CO.CH(COOC_2H_5)$ and $-C(OH)C(COOC_2H_5)$. Now Lehmann[1] has shown that many of these tautomeric derivatives of succino-succinic ether also exhibit di- and trimorphism, and that these different crystal forms may be readily changed one into the other by changing the external conditions. Hantzsch and Hermann endeavor to connect these different crystal forms with the different desmotropic conditions. Thus they say for the atom system $C_6O_2H_4(COOC_2H_5)_2$ there are three possible desmotropic conditions and three physically different forms. They assume that those forms having color belong to the group of quinones, since Graebe and Liebermann have shown that bodies belonging to the group of the quinones have color; and thus they deduce the following formulas:



$$X = (COOC_2H_5).$$

Nef[2] asserts that this question of color is purely arbitrary and proves nothing whatever regarding the structural formula of the substance, and then he shows that the third modification of ethyl p-dihydroxy-terephthalate to which Hantzsch and Hermann give the hydroquinone formula (III.) is *not* colorless, but has quite a marked color. He states that the only chemical evidence brought forward by Hantzsch and Hermann in favor of the tautomerism of hydroquinone compounds is the fact that ethyl tetra-

[1] Zeit. für Krystallog. **10**, 344. [2] This Journal **11**, 1; **12**, 379.

oxyterephthalate and ethyl quinone-dioxyterephthalate form dioximes with hydroxylamine. From the method of formation of these substances and careful analyses Nef shows them to be oxyammonium salts and *not* oximes. "There is, therefore," he continues, "absolutely no reason for assuming the existence of tautomerism or desmotropic conditions in the succino-succinic acid series. The polymorphism in this group is probably due to physical isomerism, just as has been so conclusively shown by Larsen[1] to be the case with the hydroxamic acids." Nef regards ethyl succino-succinate as nothing but dihydro-dioxyterephthalic ether (formula III.), and explains the reaction with phenylhydrazine as forming not a hydrazone, as would be the case with a ketone, but as forming a hydrazide in accordance with the equation:

$$C_6X_4\begin{matrix}OH\\OH\end{matrix} + \begin{matrix}H\\H\end{matrix}N-NHC_6H_5 = C_6X_4\begin{matrix}NH-NHC_6H_5\\NH-NHC_6H_5\end{matrix} + 2H_2O.$$

Hydrazide.

The reaction of phloroglucin with phenylhydrazine, as shown by Von Baeyer,[2] is in favor of this view, a hydrazide being formed here also.

Nef doubts the existence of tautomeric or pseudo-forms altogether, and says that, "In order to explain the behavior of such tautomeric substances the assumption has to be made that, according to the reagent acting on them, the hydrogen is bound either to carbon or to oxygen. Such an explanation has unquestionably much against it, and, especially since it attacks the foundation of modern structural chemistry, it is of the utmost importance that the most convincing proofs be brought forward to justify it."

In a later article Nef[3] takes up the question of the constitution of aceto-acetic ether. He concludes from its chemical conduct that the sodium compound of aceto-acetic ether must have the following formula:

$$CH_3-CONa=CH-CO_2R,$$

the sodium being joined to carbon by means of oxygen. To the free aceto-acetic ether Nef gives the hydroxyl formula:

$$CH_3-COH=CH.CO_2R,$$

regarding it as β-oxycrotonic acid ether. The reaction with phenylhydrazine or with hydroxylamine is, according to him, no longer sufficient to establish the ketone nature of aceto-acetic ether, since it has been shown that phenols react with amines, with phenylhydrazine or with hydroxylamine as readily as aldehydes or ketones do. Assuming the hydroxyl formula for aceto-acetic ether, the first product of the action of phenylhydrazine must be a hydrazide having the following formula:

[1] Ann. Chem. (Liebig) **253**, 170. [2] Ber. d. chem. Ges. **22**, 2189.
[3] Ann. Chem. (Liebig) **266**, 52.

$$\begin{array}{l} \mathrm{NH-NHC_6H_5} \\ | \\ \mathrm{CH_3-C=CH-CO_2R.} \end{array}$$

This would then yield a pyrazolon derivative,

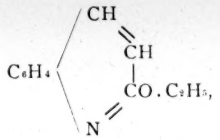
$$\begin{array}{l} \qquad\quad \mathrm{NH} \\ \qquad\quad / \qquad \backslash \\ \mathrm{CH_3-C} \qquad \mathrm{N.C_6H_5}\ , \\ \qquad\quad \| \qquad\quad | \\ \qquad\quad \mathrm{CH-CO} \end{array}$$

in which there is an imido group which should have acid properties. If, on the other hand, the ketone formula be the correct one, then a hydrazone must be the first product of the reaction between aceto-acetic ether and phenylhydrazine, and it is difficult to see how this could yield a pyrazolon derivative with an acid imido group.

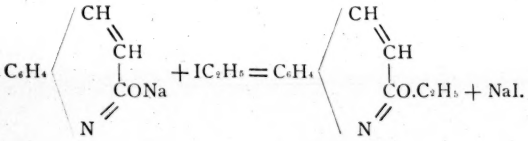
Nef has not only succeeded in isolating the hydrazide in solid condition and in showing that like hydrazobenzene it yields an azo-derivative (phenyl-β-azocrotonic acid ether) on oxidation with mercuric oxide, but he has also shown that the pyrazolon derivative, made from the hydrazide, has strong acid properties, owing to the presence of the imido group. The fact that aceto-acetic ether or the methyl or ethyl derivative can be perfectly smoothly converted into their sodium salts without any reduction of the aceto-acetic ether taking place, shows plainly, according to Nef, that these substances are not ketones. Further, he states that a methylene group (CH_2) between two carbonyl groups does *not* possess acid properties, as it would be necessary to assume if the ketone formula be accepted for aceto-acetic ether, and he cites in proof of this statement the cases of malonic acid ether, $C_3H_4O-CO-CH_2-CO-OC_2H_5$, as well as the ether of acetylene tetracarbonic acid, $\begin{array}{l} \mathrm{H_5C_2O-OC.CH.CO-OC_2H_5} \\ \qquad\qquad\quad | \\ \mathrm{H_5C_2O-OC.CH.CO-OC_2H_5} \end{array}$. Neither of these substances has acid properties. "It is accordingly," continues Nef, "highly probable that the free aceto-acetic ether is β-oxycrotonic acid ether, $CH_3-C(OH)=CH-CO_2R$, and the mono substituted aceto-acetic ethers are alkyl derivatives of β-oxycrotonic acid ether, $CH_3-C(OH)=CR-CO_2R$. These bodies show no tautomerism or desmotropism, and the assumption of a pseudo-ketone formula, according to our present knowledge, is just as little correct here as in the case of the succino-succinic ether; for the hydroxyl formula is sufficient to explain all the reactions of this body, especially all the condensations which have been brought about with it."

Having thus shown that tautomerism probably does *not* exist in the case of aceto-acetic ether and derivatives, as well as with the succino-succinic ether and derivatives, Nef next takes up the case of

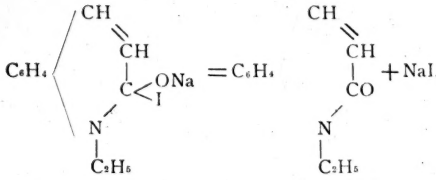
carbostyril. Friedländer and Weinberg[1] have shown that the silver salt of carbostyril, when treated with ethyl iodide, gives exclusively an oxygen ether,



while the sodium salt of carbostyril treated in the same way yields a mixture of equal parts of the oxygen and nitrogen ethers, according to the equations:



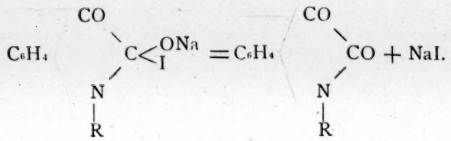
Oxygen ether.



Nitrogen ether.

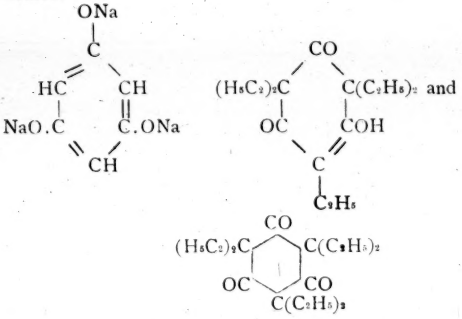
The direct replacement of the sodium by the ethyl group when the sodium salt of carbostyril is treated with ethyl iodide appears to be much more difficult, on account of the strongly positive nature of the sodium. An addition of the elements of ethyl iodide takes place, therefore, at the same time that the sodium is replaced, and there results a mixture of the two ethers. Knorr[2] has found that γ-methyl-carbostyril sodium also yields a mixture of the oxygen and nitrogen ethers when treated in the same way. Isatin shows the same conduct. Baeyer and Oekonomides have shown that the silver salt of isatin reacts with alkyl iodides to form exclusively the oxygen ethers. The sodium salt, however, according to Comstock and Kleeberg, yields only (?) the nitrogen ether, an addition of the constituents of ethyl iodide first taking place, thus

[1] Ann. Chem. (Liebig) **238**, 175. [2] Ibid. **236**, 87.



The assumption that the silver salt is differently constituted from the sodium salt is very improbable, since in many cases from both salts the same ether results.

The same explanation holds for cases of desmotropism among the phenols reported by Herzig and Zeisel. Thus the sodium salt of phloroglucin is converted by ethyl iodide into penta-ethyl and hexa-ethyl phloroglucin, an addition product being first formed.



The formation of these compounds makes it exceedingly probable that there are three cases of double union in the benzene molecule.

While silver cyanide, $Ag-N=C$, generally forms with alkyl iodides isonitriles, $R-N=C$, a direct replacement of the metal taking place, potassium cyanide, $K-N=C$, forms as a rule alkyl cyanides when treated in the same way, an addition product, $K-N=C(I)-R$, being first formed and then the organic cyanide, by the splitting off of potassium iodide. It should be noted that isonitriles sometimes result from potassium cyanide, $K-N=C$, as for example when the cyanide is treated with salts of the alkyl sulphonic acids. In this case, as in the case of the silver cyanide, $Ag-N=C$, a direct replacement of the metal probably takes place.

Nef concludes his article by saying: "It appears, therefore, to

me that the conception of tautomerism and desmotropism, as well as the conception of unstable or pseudo-forms which have become so general in organic chemistry, are by no means justified, and owe their origin to inexact knowledge of the reactions which take place in such cases." W. R. ORNDORFF.

OUTLINES OF THEORETICAL CHEMISTRY. By LOTHAR MEYER. Translated by P. Phillips Bedson and W. Carleton Williams. With a preface by the author. London: Longmans, Green & Co., 1892.

A notice of the original book of which we now have this English translation appeared in the last volume of this journal (Vol. 13, p. 429). The translators have already rendered English-speaking chemists a good service in preparing their edition of Lothar Meyer's "Die modernen Theorien der Chemie," and it appears from an examination of this new volume that they have shown the same care in its preparation as in that of the larger book. Further, as we are told, "the revised sheets have been submitted to the author."

The object of the book is expressed by the author in his preface as follows: "In writing this work I have not considered the requirements of students alone, but have been desirous of offering something to those friends of scientific investigation who have neither the intention nor the time to concern themselves with the details of chemical investigation, but wish to become acquainted with the general conclusions arrived at." I. R.

A DICTIONARY OF CHEMISTRY. By T. E. THORPE, B. Sc. (Vict.), Ph. D., F. R. S., assisted by eminent contributors. In three volumes. Vol. 2. London and New York: Longmans, Green & Co., 1891.

The first volume of this extremely valuable work appeared in 1890 and it was noticed in Volume 12, p. 280. All who have had occasion to use the first volume will welcome the second, which is "like unto it" in everything that one seeking information on subjects in the field of applied chemistry can ask for. It begins with Eau de Cologne and ends with Nux Vomica. Among the longer and more important articles included in it are the following: Fuel, by B. H. Brough; India-rubber, by C. A. Burghardt; Glycerin, by W. Lant Carpenter; Matches, by E. G. Clayton; Explosives, by W. H. Deering; Fermentation, by Percy F. Frankland; Indigo, Lakes, Litmus, Madder, by J. J. Hummel; Furfurol, Hydrazone coloring matters, by Francis R. Japp; Leather, by H. R. Proctor; Glass, by W. Ramsay; Emery, Fire-clay, Granite, Jade, etc., by F. W. Rudler; Gum-resins, Mucilage, Musk, by Alfred Senier; Iodine, by E. C. C. Stanford; Iron, by Thomas Turner; Artificial manure, Nitrification, by R. Warington; Indamines and Indophenols, by Otto N. Witt; Coal Gas, by Lewis Wright.

The closing paragraph of the notice of the first volume applies with equal force to the second: "The chemist, whether engaged in technical work or not, will find the book of great value, and he will hardly look for information without finding it. There is, in fact, no other book in English or in any other language that gives as fresh and as reliable information on subjects connected with industrial chemistry." I. R.

HÜLFSBUCH ZUR AUSFÜHRUNG CHEMISCHER ARBEITEN FÜR CHEMIKER, PHARMACEUTEN UND MEDICINER. Von Dr. HUGO SCHWANERT. ordentlichem Professor der Chemie an der Universität Greifswald. Dritte umgearbeitete Auflage. Braunschweig: C. A. Schwetschke und Sohn. 1891.

This book has long been known and has proved of value to many in the laboratory. In the new edition it is brought down to date. It has to deal with the methods in use in analytical laboratories, the subject-matter being taken up under the following heads: I. Analytic investigations of inorganic substances; II. Analytic investigations of organic substances; III. Systematic course of an analytic investigation; IV. Separation of the elements of the different groups; V. Preparation and testing of chemical preparations; VI. Gravimetric investigations; VII. Volumetric investigations; VIII. Investigation of water and articles of food; IX. Detection of poisons and blood; X. Zoöchemical investigations.

As will be seen, the book covers more ground than is usually covered by treatises on analytical chemistry, and yet everything is included within 394 pages. Obviously no single subject can be treated very fully. In a great many cases, however, "just what is wanted" will be found. I. R.

LABORATORY PRACTICE, A SERIES OF EXPERIMENTS ON THE FUNDAMENTAL PRINCIPLES OF CHEMISTRY, A COMPANION VOLUME TO THE NEW CHEMISTRY. By JOSIAH PARSONS COOKE, LL. D. New York: D. Appleton & Co., 1891.

Anything written by Professor Cooke on the subject of chemistry must be of interest to chemists, and especially is this true of anything touching the methods of teaching the elements of chemistry, an extremely difficult subject, and one to which Professor Cooke has given much attention. The book before us contains directions for a number of comparatively simple experiments in chemistry and physics. It differs markedly from many books having the same object, in that it does not attempt to "teach all the principal facts of the science in six weeks." The number of experiments described is small, but the work required in each

case involves the expenditure of some time, so that each experiment is thus more likely to make a lasting impression. The very important truth is recognised that it is better to teach a few things well than many superficially. In the introduction the author says: "This book is not intended to be used without a teacher." . . . "The educational value of such a course as is here outlined depends entirely on the manner in which the work is directed and supervised. The student should be instructed, by continued reiteration, if necessary—

1. To observe the minutest particular in regard to every experiment.
2. To distinguish essential from non-essential phenomena.
3. To draw correct inferences from the results.
4. To express concisely but clearly in writing the facts observed and conclusions reached."

The more frequently these words of caution are brought to the attention of teachers the sooner shall we reach the stage when laboratory courses will have educational value. It is certainly true that at present many sins are committed under the name of "teaching elementary science."

I. R.

METHODS OF GAS ANALYSIS. By Dr. WALTHER HEMPEL, Professor of Chemistry in the Dresden Polytechnicum. Translated from the second German edition by L. M. DENNIS, Assistant Professor of Analytical Chemistry in Cornell University. 8vo. Macmillan & Co., London and New York, 1892.

The subject of gas analysis has become, at the present time, so important, both from a scientific and a technical point of view, that the appearance of an English translation of this book by so competent an authority and investigator as Professor Hempel will be welcomed by all English-speaking chemists. The translation is practically a revision of the second German edition under the direction of the author and by one of his pupils. Several of the illustrations have been changed and improved, all the data have been revised and brought up to date, new methods which have been tried and found to work satisfactorily have been introduced, and the English edition is really better than the present German one. All references are given, and care seems to have been taken to verify these as well as all the equations made use of. Some of the formulas of the German edition have been corrected, and tables giving the atomic weights, the reduction of a gas volume to 0° and 760 mm., the tension of aqueous vapor, and the theoretical densities and the weights of one liter of the gases, all of which will be of great use to the student, have been added to the English edition. A full and complete index which includes all authorities cited is another point in which the English translation is superior to the German edition.

The book is singularly free from all kinds of errors, is well printed and bound, and is of convenient size and shape for a text-book and laboratory manual. The illustrations, of which there are quite a number, are neat and well drawn, the type clear and of a size easy to read.

The translation is in clear and forcible English and true to the original. The contents are divided into three parts. Part one has to do with the general methods of gas analysis, including the collection and keeping of gases, and a description of the apparatus, laboratory, and appliances used in both technical and exact gas analysis. Part two is taken up with the special methods of gas analysis, and part three with the practical applications of gas analysis to the analysis of furnace gases, illuminating gas, etc., etc. Altogether the work is an admirable exposition of the subject and one that no analytical chemist can afford to be without.

W. R. O.

A TEXT-BOOK OF ELEMENTARY CHEMISTRY, THEORETICAL AND INORGANIC. By GEORGE F. BARKER, M. D. Second edition, revised and enlarged. Louisville, Ky.: John P. Morton & Co., 1891.

The first edition of this book appeared at a time when the chemists of this country were learning to accustom themselves to what is generally somewhat vaguely called "Modern Chemistry," the chemistry which is founded upon Avogadro's law, the new atomic weights and our present conceptions of valency and constitution, and Professor Barker did the country a service in bringing the new ideas in elementary form before chemists. His book has been used extensively and has been helpful to many. In regard to the second edition now before us the author says: "The gratifying success achieved by the first edition of this book seems to make it undesirable, in revising it, to alter materially its general plan. In this edition, therefore, the framework has been allowed to remain in much the same form as that in which it was originally constructed." The periodic law is made the guide in the classification of the elements, and in general the treatment is up to the times.

I. R.

LEHRBUCH DER TECHNISCHEN CHEMIE. Von Dr. H. OST, Professor der Technischen Chemie an der Technischen Hochschule zu Hannover. Berlin: R. Oppenheim, 1890.

Prof. Ost's book is a volume of 700 pages with 200 woodcuts: the type and illustrations are excellent. It is a concise, clearly written text-book for students of technical chemistry. It includes descriptions of the latest improvements and discoveries in this branch, and can be cordially recommended as a book for study.

E. R.

HANDBUCH DER PHOTOGRAPHIE. Von PROF. DR. H. W. VOGEL, Vorsteher des photochemischen Laboratoriums, der Königlichen technischen Hochschule Berlin-Charlottenburg, Herausgeber der Photographischen Mittheilungen. Vier Theile, enthaltend Die photographische Chemie, Optik, Praxis und Aesthetik. I. Theil. Photochemie und Beschreibung der photographischen Chemicalien. Vierte, gänzlich umgearbeitete, verbesserte, und vermehrte Auflage. Verlag von Robert Oppenheim: Berlin, 1890. 351 Seiten. 8vo.

This belated notice has too long been due Professor Vogel's book. No one is better qualified than the author to treat of anything in the realm of photography, an art which he has done so much to advance to its present high condition. All who are interested in the chemical side of photography should have this book available for reference. It is written with true German thoroughness, and the subject is dealt with in the true scientific spirit. It goes without saying that the matter is brought up to date in this new edition. Water taken direct from the spring is pretty sure to be fresh.

I. R.

MANUAL OF CHEMICAL TECHNOLOGY. By RUDOLF VON WAGNER. Translated and edited by WILLIAM CROOKES, F. R. S., from the thirteenth enlarged German edition as remodeled by Dr. Ferdinand Fischer. With 596 illustrations. D. Appleton & Co., New York, 1892. 968 pp.

This is a large volume of 950 closely printed pages with about 600 woodcuts. This useful book of reference covers the whole field of applied chemistry. Fuel, lighting, metallurgy, the manufactures of inorganic and organic chemical products, glass and earthenware, articles of food, and the technology of fibres, including dyeing and tissue-printing, are treated briefly but clearly. The chapters on fuel, on the metallurgy of iron, silver, and gold, are very good.

A section by the editor on the qualitative examination of coloring matters completes the excellent chapter on the benzene dyestuffs; that on dyeing and tissue-printing is equally good. On the whole the editor has brought the book well up to date; an exception is the article on aluminium, in which no mention is made of working electric processes for obtaining pure aluminium, though the Cowles process for making alloys is described. There are works at Neuhausen on the Rhine where aluminium is made by electricity, and in this country pure aluminium, made in quantity by the Hall process in Pittsburgh, has been on the market for three years at prices much lower than those asked for aluminium formerly.

The woodcuts are printed from well-worn German blocks, lettered in sometimes nearly illegible German script, necessitating a translation of the German words with the cuts. These are minor drawbacks. The work is of great value to all interested in chemistry, metallurgy or manufactures.

E. R.

GRUNDLAGEN DER CHEMIE. Von D. MENDELEJEFF, Professor an der Universität in St. Petersburg. Aus dem Russischen übersetzt von L. Jawein, Docent am Technologischen Institut in St. Petersburg, und A. Thillot, Assistant am chemischen Laboratorium des Technologischen Instituts in St. Petersburg. Carl Ricker: St. Petersburg, 1891. (Lieferungen 2–8.) 1126 pp. 8vo.

THE PRINCIPLES OF CHEMISTRY. By D. MENDELÉEFF. Translated from the Russian (Fifth edition) by George Kamensky, A. R. S. M., of the Imperial Mint, St. Petersburg; edited by A. J. Greenway, F. I. C., subeditor of the Journal of the Chemical Society. In two volumes. Longmans, Green & Co., London and New York, 1891.

When the first number of the German translation of Mendeléeff's work appeared, about two years ago, attention was called to it in this Journal in appreciative terms. Now the work is complete, and it is clear that it abundantly fulfills the promise of the first number. As was said in the earlier notice: "Every teacher and every advanced student of chemistry should read and study this book with care. Even the most experienced will find much in it that will prove of value to him."

All the world knows that Prof. Mendeléeff has marked originality, and it is not surprising that his book is not cast in an ordinary mould. Everything that one could expect to find in a book of this size is probably to be found here, but it is, of course, in the method of treatment that the originality appears. The treatment is above all things philosophical. The writer is not satisfied with giving an account of the occurrence, preparation, and properties of a lot of substances, with a few crude suggestions in regard to their constitution. Each thing, each phenomenon suggests to him something else. If the particular thought that comes to him cannot be fitted into the text proper, a foot-note appears. Foot-notes abound as in no other book on chemistry. They form probably half the contents. But they are for the most part of special interest.

In the preface to the fifth Russian edition the author uses these words: "Experimental and practical data occupy their place, but the philosophical principles of our science form the chief theme of the work. In former times sciences, like bridges, could only be built up by supporting them on a few deep abutments and long girders. In addition to the exposition of the principles of chemistry, it has been my desire to show how science has now been built up like a suspension bridge, supported by the united strength of a number of slender but firmly fixed threads, which individually are of little strength, and has thus been carried over difficulties which before appeared impassable. In comparing the science of the past, the present, and the future, in placing the particulars of its restricted experiments side by side with its aspirations for unbounded and infinite truth, and in restraining myself from yielding to a bias towards following the most attractive representation, I have endeavored to incite in the reader a spirit of inquiry which, unsatisfied with speculative reasonings alone, should subject every

idea to experiment, excite the habit of stubborn work, necessitate a knowledge of the past, and a search for fresh threads to complete the bridge over the bottomless unknown. Experience proves that it is possible by this means to avoid two equally pernicious extremes, the Utopian—a visionary contemplation which proceeds from a current of thought only—and the realistic stagnation which is content with bare facts."

Those who have made up their minds on such matters as valency and constitution will be disappointed to find that Professor Mendeléeff does not accept the common ideas on these subjects, or rather his own ideas are much less rigid than these. But whether the reader agrees in all points with the author or not, he will be led to think by what he reads, and he will recognise in every page of the book an honest, earnest effort to discover the truth.

The English translation in two handsome volumes, one of 600, the other of 500 pages, has been prepared with the coöperation of the author. A fairly thorough examination shows that much more care has been taken in the rendering than is usual in the translation of works on chemistry into English. It is probable, considering the way in which the work has been done, that the English edition is quite as satisfactory as the German. Certain it is that both are extremely interesting reading, and it will be to the great benefit of chemistry if both are widely read and studied.

I. R.

NOTES.

Wolcott Gibbs Fund for Chemical Research.

On the 21st of February Dr. Wolcott Gibbs reached the age of 70 years, and a number of his friends united in showing their appreciation of his labors by collecting a fund to be known by his name, the income of which is to be devoted to the encouragement of chemical research. This fund, amounting to $2650, was put at the disposal of Dr. Gibbs, and an address presented to him on the morning of his birthday. The address, which was signed by one hundred and ten persons, is here given:

"The twenty-first of February, 1892, is not alone a day of importance to yourself and those nearest you, but it is also a day of rejoicing to us, who love you as a friend and comrade in the walks of life and science, and revere you as a teacher and leader in the love of truth.

It is rarely given to a man to look back from his seventieth birthday upon a lifetime devoted to the duties of patriotic citizenship and to the advancement of human knowledge, both by

important discoveries and by imparting the spirit of scientific research to others. That this usefulness may continue undiminished for many years is the heartfelt wish with which we offer our congratulations.

Between the time when you first began your scientific career and to-day, a great change has come over Chemistry in America. Then there were not many institutions which could boast of a professorship in pure chemistry, and laboratory research was denied to all but a favored few; now laboratories exist throughout the country, in which earnest work is being accomplished—in not a few by men whose ardor was first kindled by you.

But, although we have the apparatus for research, the means to encourage it are still inadequate, and it is towards supplying this want that we must direct our hopes in the future. How appropriate is it, then, to mark, by a distinct step in this direction, the birthday of one whose efforts have played so conspicuous a part in what has already been achieved!

We therefore unite in establishing a fund for the encouragement of chemical research, to be known by your name, in memory of this day, and we request you to entrust it to such hands and couple it with such conditions as you may deem best. To this end we have gladly contributed our offerings, and, although the result is a measure of our several means rather than of our inclinations, we trust that you will accept it as a token of the affection and good wishes of your friends, associates and pupils."

To this address Dr. Gibbs replied as follows:

"*My dear Professors Jackson and Loeb,—*

May I beg you to present to those from whom I received, a few days since, so signal a mark of friendship and good-will, my heartiest, most earnest and most grateful acknowledgment? The address which I received on my seventieth birthday, signed by more than one hundred friends, pupils and assistants, brings back my youth in recalling the names of those who now join to offer me more than mere good wishes to cheer my advancing age. Their active friendship has taken the form which was most acceptable to me—that of an endowment to assist research in my own branch of science, so that I can feel that in a certain sense my power to work will not terminate with my life. As the generosity of my friends permits me also to dispose of the manner in which the endowment shall be administered, I submit to them through you the plan which seems to me best adapted to carry out their wishes—a plan which has been fully tested in somewhat similar cases, and found to work well in practice.

I therefore propose that the fund raised for endowment shall be given to the National Academy of Sciences, to hold the same in trust, and to invest and reinvest as may be necessary or advisable.

The income or interest of the fund shall be administered by a Board of Directors consisting of three persons, of whom at least two shall be members of the Academy. The first Board shall consist of Charles Loring Jackson, Thomas M. Drown and Ira Remsen, and the Directors shall have power to fill vacancies in their own number, notifying the Academy of their action without delay. In case of the deaths of all the members of the Board, their places shall be filled by persons holding professorships of chemistry, to be appointed by a vote of the Academy. The Directors shall make an annual report to the Academy, stating the condition of the fund and the appropriations made during the year. They shall have absolute and entire control of the disposition of the income of the fund, employing it in such manner as they may deem for the best interest of chemical science.

It is my belief that the above, or a similar arrangement, is the best which can be made—that is to say, the one which is most likely to be of permanent benefit to science. I trust that it will meet with the approbation of those who have honored me with their confidence and their regard.

Sincerely yours,

NEWPORT, March 1, 1892. WOLCOTT GIBBS."

At the meeting of the National Academy of Sciences held in Washington, April 19–22, the fund was accepted, and a resolution was adopted expressing high appreciation of the act of Dr. Gibbs in entrusting the fund to the Academy. I. R.

Stas.[1]

In the death of Prof. JEAN SERVAIS STAS, in Brussels, on the thirteenth of December, 1891, chemistry has lost one of its greatest and best known servants.

Born in Louvain in 1813, of poor parents, his student years were a prolonged struggle against difficulties. He, however, studied medicine and took the degree of M. D.; nevertheless, he felt that his bent was toward chemistry. When, before taking his degree, he had, in 1835, in conjunction with De Coninck, investigated the root-bark of the apple tree, he had been able to isolate a new crystalline substance, phloridzine, and to describe its properties. At this time there were only two laboratories where organic chemistry could be studied—that of Liebig at Giessen, and that of Dumas in Paris. Stas chose the latter, and determined to continue the study of phloridzine in the laboratory of Dumas. Permission so to do was obtained after much difficulty, and the completion of the investigation of phloridzine called forth from Berzelius the following criticism: "We may expect much of a savant who enters the field of science with such a piece of work."

[1]Abstracted from the address of Prof. A. W. v. Hoffman: Ber. d. chem. Ges. **25**, 1. See also note, This Journal **13**, 430.

That Dumas recognised the ability of his pupil is evident, for the next work of Stas was in conjunction with his teacher—a study of the action of soda-lime upon the alcohols. In the course of this work they applied the method of fusion with caustic potash to a large number of substances, showing that in every case the alcohol yielded the corresponding acid. That fusel-oil should yield an acid identical with the natural valeric acid was at that time of particular interest. Dumas and Stas made determinations of the vapor-density and molecular weight of valeric acid, and, from the fact of its formation from fusel-oil, concluded that the latter must be an alcohol, a view they were able to establish by the preparation of valeric aldehyde from fusel-oil by oxidation.

Their next work in common was the celebrated determination of the atomic weight of carbon, carried out with a care that can hardly be excelled. Berzelius had accepted the figure 12.24, based upon an investigation conducted by himself with Dulong; the work of Dumas and Stas led to the adoption of the figure 12, and this change they justified by careful analyses of carbon compounds of known composition.

An important result of this work was that, with the simple atomic weights H = 1, C = 12, N = 14, O = 16, Prout's Hypothesis—then nearly forgotten—was revived. Stas undertook a revision of the atomic weights of many elements, with the firm conviction that the figures obtained would, as in the case of carbon, prove to be whole multiples of the atomic weight of hydrogen. At the end of this his most famous work—an investigation requiring many years for its completion—he declared the hypothesis "all pure illusion." The work of preparation for these studies was full of difficulty: to obtain glass and porcelain which would withstand the action of chemical reagents was almost impossible. To prepare pure compounds from which the atomic weights could be deduced, new methods had frequently to be devised and proved reliable. Stas followed next with his masterly work upon the question of the invariable composition of chemical compounds. He showed that the proportions in which elements unite are for a given compound absolutely definite, and are determined by the nature of the combining elements, and in no way by outside influences, such as pressure or temperature. The atomic weights deduced by him are the following [H = 1.000]: Li = 7.004, N = 14.009, O = 15.960, Na = 22.980, Cl = 35.368, K = 39.040, Br = 79.750, Ag = 107.660, I = 126.533. No serious attempt has since been made to revive Prout's hypothesis.

Stas' last great investigation was undertaken with the view of deciding upon the trustworthiness of the statement of Lockyer, that the spectra of the metals of the alkaline earths are changed at high temperatures, whence it was concluded that these metals are not true elements. Stas spent eleven years in preparing pure compounds of silver, sodium, potassium, lithium, calcium, barium, strontium, and thallium, and in repeating Lockyer's experiments

with these preparations. He showed that even at the melting-point of iridium (2200°–2500°) the spectra remained unchanged. The important studies made at this time on the spectra of the metals and that of the sun are to be found in an address, "De la nature de la lumière solaire," delivered before the Belgian Academy of Sciences.

Among Stas' minor work may be mentioned the method for the determination of the presence of alkaloids, as in cases of poisoning.

Stas was for twenty years professor in the Military School at Brussels, and was at one time connected with the mint. The fiftieth anniversary of his membership in the Belgian Academy was celebrated in 1891. He died full of years and honors, all Europe having united to show its appreciation of a life devoted to the highest interests of science.

At the meeting of the Belgian Academy of Sciences, March 6, 1892, Professor W. Spring presented a report upon the posthumous scientific papers of Stas.[1] Of these, about 1500 pages had proved to be of value. These would naturally fall into three important treatises. The first, with the title "On Silver," was called forth by the well-known investigation of Dumas, upon the power of silver to occlude gases, as well as by the doubt cast upon the conclusions drawn by Stas with regard to the value of Prout's hypothesis. With the greatest pains Stas prepared absolutely pure silver, in which no occluded gas nor any trace of other foreign matter could be detected. The metal could even be volatilised at the melting point of iridium without giving evidence of the slightest trace of sodium when examined with the spectroscope. The atomic weight of silver was still to be represented by the figure which had been determined by Stas as the result of his earlier investigation. The objections of Dumas in no respect took away from the value of Stas' former work.

The second treatise had to deal with the subject referred to above in connection with the mention of Lockyer's hypothesis.

The third treatise was on a fresh determination of the stoichiometrical relation between silver chloride and potassium chloride. The fact that he would be able to conduct the investigation with absolutely pure material was a strong incentive to undertake the work, laborious as it promised to be. Twelve different determinations agreed with one another in the most astonishing way. Although the atomic-weight determinations—as, for example, of barium, calcium, strontium, and thallium—were not included, yet these last researches of the great analyst will be gratefully welcomed, since not only do they introduce to us a mass of new material of value for the solution of important questions, but they are and must ever remain a standard for exact chemical investigation.

E. R.

[1] From the Chemiker-Zeitung, March 12, 1892.

Hermann Kopp.

Close upon the death of Stas has followed that of Hermann Kopp. The lives of the two men furnish material for an interesting comparison. Both were throughout life devoted with singleness of purpose to the study of chemistry, yet in different ways. Kopp will always be especially remembered on account of the infinite pains with which he has examined into the records of the work of ancient Philosopher and mediæval Alchemist, the Phlogistonist of former centuries and the Chemist of this, and the zealous care with which he has endeavored once for all to record their claims to the gratitude of later ages; while Stas, with equal patience and marvellous skill, has placed on a firm foundation those fundamental laws of chemical science upon which all future investigations must, at least in great degree, ultimately lean for support. Not that Kopp was a student of the history of chemistry only, but his achievements in that field were so remarkable as to throw rather into the background his only relatively less important experimental investigations.

Kopp was born in 1817. His father was a physician, a man of unusual ability, with an intense interest in scientific knowledge, which was inherited by his son. The latter entered Heidelberg to study under the direction of Gmelin, and from thence moved to Marburg, from which university he was graduated as doctor in 1838. His next move was to Giessen, where the life-long friendship which existed between Liebig and himself was developed. Wöhler, too, soon after joined them, as well as many others who have given evidence to the world of the masterful influence of Liebig over all who approached him. Kopp's work soon began to be concentrated in the department of physical chemistry. In 1841 he was made Privatdocent, and in 1843 Professor in the University, and in Giessen he remained until 1863, when he accepted a professorship in Heidelberg. From this post he could never be enticed away; his devotion to his friends—a life-long characteristic of the man—as well as the charm of life in the romantic old city, always made him strong to refuse the offers made by other universities, and in Heidelberg it was that he died.

Kopp may be considered the pioneer in certain departments of chemical research. Thus his name will always be connected with the development of our knowledge of the dependence of the physical properties of substances upon their chemical composition. His researches upon the specific volume of elements and compounds are perhaps the most famous. Among others might be mentioned his study of the relation between boiling points and chemical composition in the hydrocarbons and their derivatives; his investigation of specific heat and the changes in the volume of substances under the influence of heat, and on melting; his research into the relation of crystalline form to specific volume.

In the last he established the fact that isomorphous substances, with few exceptions, not only show, as Mitscherlich had proved, similar chemical composition, but also the same molecular volume. Kopp was also one of the first rightly to explain the abnormal vapor-densities characteristic of ammonium chloride, phosphorus pentachloride, chloral hydrate, etc.

Hermann Kopp possessed in a remarkable degree the power of acquiring a knowledge of languages: this talent he applied most successfully in his researches in the history of chemistry, afterwards to be given to the world in the famous "Geschichte der Chemie." It is unnecessary to commend the immense labor and absolute thoroughness which its author employed in the preparation of this great work; suffice it to say that it forms the groundwork upon which our present histories of chemistry are all based, and that it probably will always be regarded as a masterpiece in the department to which it belongs. Although published fifty years ago, no revised edition has since appeared; the many monographs, however, which its author has from time to time composed are known to have been intended as chapters in a second edition.

Much of Kopp's work was that of an editor. On the death of Berzelius in 1848 he joined Liebig in the publication of the Jahresbericht. This post of editor he held in common with Liebig until 1857, when the latter withdrew, and afterward with Will until 1862. In the year 1851 he joined Liebig and Wöhler in the editorship of the Annalen, after that journal had been in course of publication nearly twenty years. From that time until his death he was a member of the editorial staff, and as such his name appears on the title-pages of fully two hundred successive volumes.

At the meeting of the German Chemical Society, on February 22d, Prof. v. Hofmann delivered a touching address[1] in memory of Hermann Kopp. The writer of this notice has made use in its preparation of certain details there given. W. W. R.

T. Sterry Hunt.

Dr. T. Sterry Hunt died in New York, February 12, 1892, in his 74th year. He studied chemistry at Yale and was in 1845 made Assistant to Prof. Silliman. In 1847 he was appointed chemist and mineralogist to the Geological Survey of Canada. From 1856 to 1872 he was Professor of Chemistry at Laval University at Quebec and at McGill University at Montreal, successively. From 1872 to 1878 he occupied the position of Professor of Geology at the Massachusetts Institute of Technology. In 1881 the degree of LL. D. was conferred upon him by the University of Cambridge.

[1] Ber. d. chem. Ges. **25**, 505.

The most valuable of Dr. Hunt's scientific writings may be divided into two groups: (1) those published when a member of the Geological Survey of Canada, and (2) his more or less speculative chemical papers. In the latter he early showed a sympathy with the aims of Gerhardt, and in a series of articles in the American Journal of Science enthusiastically advocated the methods used by the French chemist in his efforts to systematise the classification of chemical substances. In his endeavors to extend the views of Gerhardt he showed himself considerably in advance of most of the chemists of his time. Among his more important chemical papers may be mentioned his "New Basis for Chemistry," "Theory of Chemical Change and Equivalent Volumes," "Chemical and Geological Essays," "Solution and the Chemical Process," "The Foundations of Chemistry," "Mineral Physiology," etc., etc.

In all his speculations he was inclined to take a radical position, and although many of his conclusions would seem to have been justified by the facts, yet it must be remembered that his opinions were frequently characterised by recklessness and narrowness of view.

During the last few years the decline of his health has necessitated his withdrawal, at any rate to a great extent, from active scientific discussion. W. W. R.

Wilhelm Dittmar.

Wilhelm Dittmar, Professor of Chemistry in the Technical College at Glasgow, died February 9, 1892. He was born in 1833 in Hesse, entered Bunsen's laboratory in 1857, and, after serving some while as assistant, moved to England to occupy a similar position in the laboratory of Roscoe when the latter was appointed to the professorship in the Owens College, Manchester. Between 1861 and 1869 Dittmar served Playfair in the same capacity, after which he returned to Germany. Three years later he became assistant to Professor Crum Brown, was then appointed to a professorship in the Owens College, and, finally, accepted the position of Professor of Chemistry in Glasgow.

Two of Dittmar's more important investigations were the study, with Roscoe, of the chemical relations existing between hydrochloric acid and water, and that upon the process of distillation *in vacuo*.

On the Preparation of Formic Acid.

If in the manufacture of formic acid the mixture of oxalic acid and glycerin is heated on the water-bath, the operation is a very slow one, but on heating but a few degrees above the boiling-point of water the yield in a given time is quite satisfactory. Equal quantities of glycerin and oxalic acid are put into a retort or distilling-

flask and this placed in an oil-bath which is heated to 120°. The temperature of the mixture rises slowly to 105°–107°, and there remains for quite a time, while formic acid distils over. It then rises to 112°, again shows a tendency to remain constant, and then again rises. When it reaches 115°, the mixture should be allowed to cool to 65° or 70°, the same quantity of oxalic acid added, again heated, and so on. After the third or fourth addition of oxalic acid, 55 per cent. formic acid distils over in theoretical quantity and, if the temperature of the oil-bath is kept below 125°, this acid is free from allyl alcohol and cannot be distinguished from the acid prepared at a lower temperature. In my work I used 300 grams of glycerin in a retort or flask of 1000–1200 cc. capacity. With the water-bath less than 100 grams dilute formic acid were obtained, whereas with the oil-bath 900 to 1200 grams oxalic acid were used daily, yielding the second day 550 to 775 grams formic acid, sp. gr. 1.135. FELIX LENGFELD.

From a letter of Dr. Wolcott Gibbs to the Editor.

"Prof. Barker has directed my attention to the fact that in my note on the electrolytic determination of metals as amalgams,[1] the date on which my paper was read before the National Academy of Sciences is given as October, 1883, while the records of the Academy show that the date was November, 1880. The inaccurate statement in my friend Prof. Edgar F. Smith's work is not due to any negligence on his part, but simply to the fact that his information was derived from the Zeitschrift für analytische Chemie and the Chemical News. The fact is that I am myself to blame for neglect to publish a full and complete statement."

[1] This Journal **13**, 510.